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Notes on the

Colorimetric Determination of pH of Surface Active Solutions of Textile Assistants

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Introduction

THERE have been two important trends in the textile industry during the past few years. One development is an increasingly careful control of the pH during the processing of textiles. A second development has been a wide application of a variety of synthetic organic products to assist in gaining such desired effects as increased wetting of and penetration into fibers, emulsification of waxes and oils and many related processes. These synthetic products are all characterized by their ability to form colloidal solutions of high surface activity, which makes possible their use as wetting, penetrating and dispersing agents. The control of the pH is usually accomplished by the colorimetric method because of the simplicity and speed accompanying its use. However, the authors (5) have shown that the presence of sulfated fatty alcohols produces appreciable errors in the colorimetric determination of pH, while the data of Burton and Robertshaw (1) show that sulfonated oils produce similar effects. Mosher (4) has proved that many indicators are appreciably in error when used for the determination of the pH of soap solutions. Recently Hartley (3) has made observations of the displacement of the indicator color by colloidal long chain salts. He suggests that this displacement of color is due to adsorption of the indicator ions by the miscelles.

A further examination was made in this Laboratory of the effect of a variety of assistants, including sulfonated oils, alkyl naphthalene sodium sulfonates, sulfonated and sulfated fatty alcohols, and modified fatty acids, on a number of common indicators. Each product tested exerts a specific effect upon the color of indicators thus causing observation of incorrect values for the pH of solutions. While the errors would be negligible for the concentration of assistants used in many processes, it is nevertheless important to emphasize the limitations of the colorimetric method.

It is the purpose of this paper to describe quantitatively the errors caused by various textile assistants upon common indicators, and to give tables which may be used for correcting observed values to satisfactory approximations of the actual pH values of the solutions. In addition, a simple method, employing dialysis through a Cellophane membrane, is described which gives a relatively accurate alternative method for the colorimetric determination of the pH of solutions containing textile assistants.

Materials

A summary of the products used in this work, together with their general chemical classification, follows:

Gardinol WA Concentrated, Gardinol CA, Brilliant Avirol L-142, and Lanaclarin LM are representatives of the sodium salts of fatty alcohol sulfates.

Brilliant Avirol L-144 is a product of sulfated oleyl alcohol.

Alkanol B is an alkylated naphthalene sodium sulfonate.

Igepon T and Igepon AP are condensation products of taurine and ethionic acid respectively with oleic acid.

Prestabit oil is a highly sulfonated oil.

All samples of the materials used were representative of commercial products.

Method for Determining Errors

The method used for determining the errors introduced by the presence of the various assistants in the colorimetric determination of pH was as follows: the pH of 5 cc. of a buffer solution, prepared according to the specifications of Clark (2), diluted with 5 cc. of distilled water, was observed colorimetrically in a block comparator. Then the apparent pH of 5 cc. of the same buffer solution diluted with 5 cc. of a solution of the textile assistant under consideration was determined in the same manner. If the true or actual pH values of the buffer solutions diluted with water and diluted with a solution of the textile

TABLE I

Effect of Gardinol WA Concentrated, Gardinol CA, and Alkanol B on Indicators

Indicator and Range	Observed pH of Buffer	OBSERVED pH OF BUFFER WITH Gardinol WA at 0.15%	Gardinol WA at 0.75%	Gardinol WA at 7.5%	Gardinol CA at 0.5%	Alkanol B at 0.1%	Alkanol B at 0.5%	Alkanol B at 2.5%	Alkanol B at 5.0%
Cresol Red	1.3	0.4	<0.2	<0.2	0.4	..	..	..	..
0.2-1.8	1.9	1.4	0.4	1.0	1.4	..	..	..	..
	2.3	..	1.3	1.4	1.8	..	..	..	..
	2.7	..	1.6	..	..	..	..	..	..
Metacresol	1.9	1.7	<1.2	..	1.7	..	..	..	..
Purple	2.1	..	..	..	..	2.1	1.9	<1.2	<1.2
1.2-2.8	2.3	2.2	1.7	1.7	2.2	..	..	..	..
	2.7	2.6	1.9	1.9	2.5	2.7	2.4	1.8	1.7
	3.0	..	..	2.3	..	..	2.7	2.3	2.3
La Motte	2.7	..	..	..	2.8	2.6	..	..	..
Yellow	3.0	2.9	<2.6	2.8	3.1	2.9	2.6	..	..
2.6-4.2	3.6	3.6	3.3	3.5	3.6	3.5	3.1	2.6	..
	4.0	4.0	3.8	3.9	4.0	3.9	3.8	2.8	2.9
	4.7	..	..	..	..	..	4.1	3.6	3.7
Bromcresol	4.0	3.9	..	..	<3.8	4.0	3.9	<3.8	..
Green	4.6	4.5	4.0	..	4.3	4.6	4.3	3.8	<3.8
3.8-5.4	5.0	4.9	4.3	<3.8	4.6	5.0	4.7	4.1	4.0
	5.6	..	4.9	4.0	5.2	..	5.3	4.6	4.5
	6.0	..	..	4.4	..	..	..	4.9	4.8
	6.4	..	..	4.5	..	..	..	..	..
	7.0	..	..	5.0	..	..	..	..	..
Methyl Red	4.7	..	4.6	..	4.6	..	..	..	..
4.4-6.0	5.1	4.9	4.7	..	4.8	..	..	..	..
	5.7	5.2	4.9	4.4	5.2	..	..	..	..
	6.0	5.6	5.0	4.6	5.4	..	..	..	..
	6.4	..	5.3	4.7	..	..	..	..	..
	7.0	..	5.7	4.9	..	..	..	..	..
	7.6	..	..	5.4	..	..	..	..	..
	8.0	..	..	5.9	..	..	..	..	..
Bromcresol	5.6	5.6	<5.2	..	5.4	5.6	5.4	<5.2	..
Purple	6.0	6.0	5.4	5.2	5.6	6.0	5.8	5.2	<5.2
5.2-6.8	6.4	6.3	5.9	5.2	6.1	6.4	6.2	5.4	5.2
	7.0	..	6.4	5.4	6.7	..	6.7	6.1	5.7
	7.6	..	..	6.1	..	..	..	6.7	6.2
Chlorphenol	5.6	5.6	5.5	..	5.5	5.6	5.5	5.2	..
Red	6.0	5.9	5.7	..	5.8	6.0	5.9	5.5	..
5.2-6.8	6.4	6.4	6.1	5.3	6.2	6.4	6.3	5.8	5.4
	7.0	..	..	5.9	..	..	6.7	6.5	6.1
	7.6	..	..	6.6	..	..	..	>6.8	>6.8
Bromthymol	6.4	6.0	..	..	..	..	..	..	..
Blue	6.6	..	..	..	..	6.6	<6.0	..	..
6.0-7.6	7.0	6.6	<6.0	..	<6.0	7.0	6.2	..	..
	7.6	7.0	6.1	..	6.5	7.6	6.7	6.0	<6.0
	7.9	..	6.5	<6.0	6.8	..	7.2	6.4	6.3
	8.7	..	..	6.4	..	..	..	7.1	7.0
	9.6	..	..	7.0	..	..	..	..	..

TABLE I—Continued

Effect of Gardinol WA Concentrated, Gardinol CA, and Alkanol B on Indicators

Indicator and Range	Observed pH of Buffer	OBSERVED pH OF BUFFER WITH Gardinol WA at 0.15%	Gardinol WA at 0.75%	Gardinol WA at 7.5%	Gardinol CA at 0.5%	Alkanol B at 0.1%	Alkanol B at 0.5%	Alkanol B at 2.5%	Alkanol B at 5.0%
Phenol Red	6.9	6.9	6.9	..	6.9	6.9	6.8	..	..
6.6-8.4	7.5	7.5	7.5	7.0	7.5	7.5	7.4	7.2	6.9
	7.9	7.9	7.9	7.6	7.8	7.9	7.8	7.5	7.3
	8.5	..	..	..	..	..	8.4	8.3	8.0
Cresol Red	7.6	7.6	..	..	7.4	7.6	7.4	<7.2	..
7.2-8.8	7.9	7.9	7.8	7.3	7.8	7.9	7.9	7.8	7.3
	8.5	..	..	..	..	8.4	8.3	7.9	7.7
	8.7	8.7	8.6	7.7	8.7	..	..	..	..
	8.9	..	..	..	..	..	..	8.4	8.0
Thymol Blue	8.5	..	..	..	..	8.4	8.0	..	..
8.0-9.6	8.7	8.4	..	..	8.1	..	..	..	..
	8.9	..	..	..	..	8.9	8.5	<8.0	..
	9.6	9.1	8.7	<8.0	8.9	9.6	9.2	8.4	8.2
	10.2	..	9.0	..	..	..	..	8.7	8.4
	10.6	>9.6	..	8.1	..	..	..	9.0	8.7
	11.0	..	..	8.5	..	..	..	..	..
La Motte	9.6	<9.6	<9.6	<9.6	9.7	..	..	..	..
Purple	9.8	..	..	..	..	9.7	9.6	..	..
9.6-11.2	10.4	..	10.4	..	..	10.4	9.7	<9.6	<9.6
	10.6	10.5	10.6	10.4	10.6	10.6	10.6	10.4	10.2
	10.8	..	10.8	..	..	10.8	10.8	10.6	10.4
	11.0	10.9	..	10.8	11.0	..	..	..	..

assistant are the same, then the difference in the two colorimetric determinations gives the error introduced by the presence of the textile assistant.

The method as outlined is based on the assumption that a solution of the buffer diluted with a solution of the textile assistant possesses the same pH as a solution of the buffer diluted with water. Potentiometric measurements using the quinhydrone electrode proved that this assumption in correct. The tests were made by immersing electrodes in solutions of the buffer diluted with water and diluted with a solution of the assistant. The two solutions were connected with a salt bridge and the circuit completed through a potentiometer. A difference of 0.1 pH between buffered solutions produced a potential difference of 8.0 millivolts between the two electrodes.

The errors introduced in buffered solutions of pH 7.0 containing 1.25% Igepon T. 10% Prestabit oil, and 10% Brilliant Avirol L-144 were less than 0.2 pH, while the errors introduced by 7.5% Gardinol WA, 0.25% Gardinol CA, 5% Alkanol B, 10% Lanaclarin LM, 0.025% Brilliant Avirol L-142, and 1% Igepon AP Extra were less than 0.1 pH. All differences in potential for solutions of one-tenth of the above concentrations corresponded to differences of less than 0.1 pH. These errors, which are small in comparison with the errors observed colorimetrically, are probably due to the salt effect. It was shown that solutions of sodium sulfate and of Gardinol WA, containing equivalent concentrations of sodium ions, show the same potential difference with the quinhydrone electrode.

Apparent Variation in pH in Presence of Textile Assistants

Colorimetric measurements were made of the pH of buffered solutions of various textile assistants, and comparisons were made by the outlined method with the pH of the buffer solutions alone. Tables I and II contain a summary of the data obtained.

The data in Tables I and II show that a variety of sulfated fatty alcohol products and an alkyl naphthalene sodium sulfonate exert a specific effect in the color change of indicators which varies both with the indicators and the products tested. Similar results in which the errors are of the same order of magnitude have been obtained with Igepon T, Igepon AP and Prestabit Oil. A variation in the error produced with different indicators may occur at different pH values covered by the indicator

TABLE II

Effect of Brilliant Avirol L-142, Brilliant Avirol L-144 and Lanaclarin LM on Indicators

Indicator and Range	Observed pH of Buffer	OBSERVED pH OF BUFFER WITH Brilliant Avirol L-142 at 0.01%	Brilliant Avirol L-142 at 0.05%	Brilliant Avirol L-144 at 0.1%	Brilliant Avirol L-144 at 0.5%	Brilliant Avirol L-144 at 2.5%	Brilliant Avirol L-144 at 10%	Lanaclarin LM at 0.1%	Lanaclarin LM at 0.5%	Lanaclarin LM at 2.5%	Lanaclarin LM at 10%
Metacresol	2.1	2.1	2.1	2.1	2.0	1.9	1.8	2.1	1.9	1.7	1.7
Purple	2.7	2.7	2.7	2.7	2.6	2.5	2.3	2.7	2.5	2.2	2.2
1.2-2.8	2.9	..	..	..	..	2.8	2.7	..	2.8	2.6	2.7
LaMotte	2.6	2.6	2.6	2.6	2.6	2.6	..	2.6	<2.6	..	..
Yellow	2.9	2.9	2.9	2.9	2.9	2.7	3.0	2.9	2.7	2.7	3.3
2.6-4.2	3.5	3.5	3.5	3.5	3.4	3.5	3.9	3.5	3.5	3.5	3.9
	3.8	3.9	3.9	3.8	3.9	3.9	>4.2	3.8	3.8	3.9	>4.2
Bromcresol	4.1	4.1	4.0	4.1	4.1	3.8	3.9	4.0	<3.8	..	..
Green	4.6	4.6	4.5	4.6	4.5	4.3	4.1	4.6	4.4	4.0	<3.8
3.8-5.4	5.0	5.0	4.9	5.0	4.9	4.6	4.4	5.0	4.7	4.3	4.1
	5.5	..	>5.4	..	5.4	5.1	4.8	..	5.3	4.8	4.5
	6.0	..	..	..	..	>5.4	5.1	..	..	5.1	4.7
Bromcresol	5.5	5.5	5.5	5.5	5.5	5.4	..	5.5	5.4	<5.2	..
Purple	6.0	6.0	5.9	5.9	5.9	5.6	<5.2	6.0	5.8	5.4	<5.2
5.2-6.8	6.5	6.5	6.5	6.5	6.5	6.2	5.9	6.5	6.3	6.1	5.5
	7.0	..	>6.8	..	>6.8	6.6	6.1	..	6.7	6.5	6.1
Chlorphenol	5.6	5.6	5.6	5.6	5.5	5.4	<5.2	5.6	5.5	5.4	<5.2
Red	5.9	5.9	5.9	5.9	5.8	5.7	5.4	5.9	5.8	5.7	5.4
5.2-6.8	6.5	6.5	6.5	6.5	6.5	6.3	5.9	6.5	6.5	6.3	5.9
	7.0	..	..	..	>6.8	6.7	6.3	..	>6.8	6.8	6.5
Bromthymol	6.0	6.0	<6.0	<6.0	..	..	..	<6.0	..	..	..
Blue	6.6	6.4	6.3	6.5	6.2	<6.0	..	6.4	6.0	<6.0	..
6.0-7.6	7.0	6.7	6.5	6.7	6.5	6.0	..	6.7	6.1	<6.0	..
	7.6	7.4	7.1	7.5	7.1	6.5	<6.0	7.4	6.7	6.2	<6.0
	7.9	..	7.3	..	7.3	6.8	6.2	..	6.9	6.5	6.3
	8.5	..	>7.6	..	..	7.3	6.6	..	7.3	7.0	6.8
Phenol Red	7.0	7.0	7.0	7.0	7.0	6.9	<6.8	7.0	6.9	6.8	<6.8
6.8-8.4	7.5	7.5	7.5	7.5	7.5	7.4	7.2	7.5	7.5	7.4	7.2
	7.9	7.9	7.8	7.9	7.9	7.7	7.6	7.9	7.9	7.7	7.6
	8.5	..	>8.4	..	>8.4	8.4	8.1	..	>8.4	8.4	8.2
Cresol Red	7.6	7.6	7.6	7.6	7.6	7.4	7.2	7.6	7.5	7.3	7.2
7.2-8.8	7.9	7.9	7.9	7.9	7.9	7.8	7.5	7.9	7.8	7.7	7.4
	8.5	8.5	8.5	8.5	8.5	8.4	8.1	8.5	8.5	8.3	8.0
	8.9	..	..	..	..	8.7	8.5	..	..	8.7	8.4
Thymol Blue	8.5	8.4	8.2	8.4	8.3	<8.0	..	8.5	<8.0	..	..
8.0-9.6	8.9	8.9	8.4	8.9	8.7	8.3	<8.0	8.8	8.4	<8.0	..
	9.4	9.4	9.3	9.4	9.3	8.9	8.3	9.4	9.2	8.5	8.0
	10.1	..	..	..	..	>9.6	8.9	..	9.6	9.3	8.9
LaMotte	10.1	10.1	10.1	10.1	10.1	10.0	10.0	10.1	10.1	10.1	10.1
Purple	10.5	10.5	10.5	10.5	10.5	10.2	10.1	10.5	10.5	10.5	10.5
9.6-11.2	10.9	10.9	10.9	10.9	10.9	10.8	10.7	10.9	10.9	10.9	10.9

range and with the exception of LaMotte Yellow the errors produced with the different indicators are on the acid side. The errors introduced by the textile assistants are influenced markedly by the concentration of the product tested. Concentrations of textile assistants as low as 0.1 per cent, produce appreciable errors with the indicators bromthymol blue and thymol blue. The presence of 0.5% of assistant in general produces errors of at least 0.2 of a pH unit and the errors frequently are greater than 1.0.

Dialysis Method for Use with Indicators

A simple method, which utilizes the principle of dialysis, has been worked out for the colorimetric determination of solutions containing sulfated fatty alcohol products and alkylated naphthalene sodium sulfonates. The method was tested with buffered solutions containing the various assistants over a pH range 5.0-9.0. It was found that the pH of solutions of these types of products can be determined by this method to within 0.1 unit of the correct value. An attempt to apply this method to solutions of Prestabit Oil was unsuccessful.

The method used was as follows: A cell was prepared by fastening a sheet of No. 500 plain, transparent Cellophane by means of a rubber band over one end of a glass tube 2.5 centimeters in diameter and 12.0 centimeters long. The tube was placed, membrane down, in a 250 cc. beaker containing about 200 cc. of the solution of the assistant. The tube was filled with distilled water to the level of the outside liquid, and was allowed to stand for a given time. At the end of this time the pH of the solution in the cell was determined colorimetrically. Table III contains the data for colorimetric measurements of the pH of solutions of textile assistants buffered at pH values of 5.0, 7.0, and 9.0 following dialysis for 1, 2, and 3 hours by the method as outlined.

The indicators used for the experiment summarized in Table III were bromcresol green (3.8-5.4), bromthymol blue (6.0-7.6), and thymol blue (8.0-9.6). During dialysis neither the color nor the turbidity of the solutions of textile assistants was transmitted to the water in the cell, indicating that the assistant was excluded to a large extent from the cell. The absence of color and turbidity also aided in obtaining more accurate readings with the indicators.

The data in Table III show that the dialysis method is satisfactory for the products listed. At pH 5.0 and 7.0, dialysis for one hour is sufficient to insure determination of the hydrogen ion concentration to within 0.1 of a pH unit; at a pH of 9.0, dialysis for three hours is required for this degree of accuracy. It is inadvisable to continue dialysis for a time much longer than this, since after prolonged dialysis sufficient of the assistant diffuses through the membrane to affect the indicators. The fact that satisfactory results are obtained by the dialysis method with indicators which are affected considerably by the presence of textile assistants in solution is conclusive evidence that the method is of value.

Acknowledgement

The authors desire to take this opportunity to express their appreciation to Dr. Samuel Lenher for his kindly interest and helpful criticisms and suggestions in connection with this work.

Summary

Textile assistants which form solutions having a pronounced surface activity exert a specific effect on indicators which may cause errors in the colorimetric determination of pH. Measurements of the effect of a variety of synthetic organic products on a number of common indicators are presented in tabular form. The data may be used for the correction of observed pH values for solutions. A simple method employing dialysis through a cellophane membrane is described for the colorimetric determination of the pH of solutions containing textile assistants.

Literature Cited

(1) Burton and Robertshaw, J. International Society of Leather Trades Chemists *18*, 19, (1934).
(2) Clark, "The Determination of Hydrogen Ions," p. 192. Williams and Wilkins Co., Baltimore (1928).
(3) Hartley, Trans. Faraday Soc. *30*, 444 (1934).
(4) Mosher, Am. Dyestuff Reptr. *19*, 261 (1930).
(5) Smith and Jones, J. Phys. Chem. *38*, 243 (1934).

TABLE III
Dialysis Method for Determination of pH

Product	Conc.	Buffer pH 5.0			Buffer pH 7.0			Buffer pH 9.0		
		1 hr.	2 hr.	3 hr.	1 hr.	2 hr.	3 hr.	1 hr.	2 hr.	3 hr.
Gardinol WA Conc.....	7.5%	5.1	5.1	5.1	6.9	7.0	6.9	8.9	8.9	8.9
Gardinol CA	0.5%	5.1	5.0	5.0	7.0	7.0	7.0	8.8	8.8	8.9
Brilliant Avirol L-142	0.5%	5.1	5.0	5.0	7.0	7.0	7.0	8.8	8.9	8.9
Brilliant Avirol L-144	10.0%	5.1	5.1	5.1	6.9	7.0	6.9	8.7	8.8	8.9
Lanaclarin LM	10.0%	5.1	5.1	5.1	7.0	7.0	7.0	8.9	9.0	9.0
Alkanol B	5.0%	5.1	5.1	5.1	7.0	7.0	7.0	8.9	9.0	9.0

Principles of Oiling and Scouring Wool

A FAIRLY recent article on emulsification contains some of the best available data on fundamental principles of oiling and scouring wool. (Speakman and Chamberlain, Transactions of the Faraday Society, 1933, page 358.) Since this information is in a journal which is not widely available and is published under a title which does not give any clew to this portion of its contents the parts of most interest to textile men will be briefly abstracted.

This discussion is based on the British practice of using mainly oleic acid as an oil in woolen manufacture and its removal very largely by soda ash; but more especially on the use of olive oil with not over 5 per cent free fatty acid for worsted. The usual amount is about 3 per cent and if this is uniformly distributed over the wool it follows from available data that the oil film will be of such a thickness (or thinness), that it will have a highly organized structure, or a particular orientation on the surface of the wool.

There will be adhesion between oil and wool, which will increase with the chain lengths of the oil molecules and their polar character. Such adhesion, and cohesion within the film, cause the oil to resist emulsification and it now seems that the emulsification of scouring is resisted by some form of molecular adhesion.

Returning to the oil used in combing with its great surface of exposure to the air and chance for oxidation, only non-drying oils can be used because the oxidized film cannot be emulsified. Olive oil has, of course, long been the favorite. In spite of cheapness and non-oxidizing character mineral oil has not been used because it could not be removed by emulsification with soap and water. The real reason for this has not previously been established.

Without going into details, the method of experiment was essentially the impregnation of worsted fabric with a uniformly distributed known weight of oil, and then a carefully controlled scouring. The method of scouring was especially worked out for its effectiveness. The oiled material was first scoured with a 2 per cent solution of soda ash and then in a new bath with 0.4 per cent soap solution. The soda satisfies the great affinity of the wool for alkali so that there will not be adsorption of alkali from the soap and formation of acid soap. Soap was used alone because in a mixture the soda may salt out the soap sufficiently to interfere with lathering. Also, the use of soap in the preliminary soda scour was found to cause practically no increase in the amount of oil removed. After the soap scour the samples were washed with water by gradual dilution so as not to break the emulsion of oil in the scouring solution. The amount of residual oil was determined later.

It was found in a comparison of various fractions of mineral oil free from unsaturated constituents that the difficulty of removal from wool increases with the boiling-point of the oil, which means, with the length of the molecule. The removal was quite incomplete, but not entirely owing to the adhesion factor. Mineral oil is non-polar and its emulsification is difficult on account of the resulting high interfacial tension.

In a group of very important experiments it was found that a very small addition of oleyl alcohol to the mineral oil before applying it to the wool made it scour out much more easily. The best proportion to use was found to be about 6 per cent. An increase beyond 7 per cent increased the difficulty of scouring and beyond 55 per cent the mixture came off with more difficulty than mineral oil alone. These results have been explained but the principal point is the striking effect at about 6 per cent, apparently due to the reduction of surface tension of the oil, which may indicate a loss of some tendency to a structure in the oil which would resist emulsification.

In contrast it was shown that about 80 per cent of olive oil had to be mixed with the mineral oil for effective removal of the oil mixture; or about 70 per cent of oleic acid which seems to serve merely as a "scourable diluent" for the mineral oil.

When soda is used there is conversion into soap when scouring begins and when the oleic acid is thus dissolved out it is simply a case of mineral oil and soap. With oleyl alcohol the alcohol remains dissolved in the oil and maintains the low interfacial tension while the soap reduces that of the water.

In spite of its high effectiveness the use of oleyl alcohol is not regarded as a complete practical solution to the problem of how to utilize mineral oil in worsted manufacture. In the experiments under discussion it left nearly 0.6 per cent of the oil after scouring when the total amount applied was 5 per cent.

From another source comes the information that 15 per cent of lanolin in mineral oil causes it to emulsify as easily as olive oil. This explains its use in lubricating oil for textile use so that spots can be readily scoured out.

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

July 30, 1934

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E. I. Du Pont de Nemours & Co., Wilmington, Del.

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H. S. Bliven, Chairman; D. B. Hardin, Secretary.

Members should notify the **Secretary** immediately of all address changes

OUTING, RHODE ISLAND SECTION

JUNE 29th, 1934, witnessed the Third Annual Outing of the Section at the Warwick Country Club, with short of one hundred members and guests present. The Outing Committee, headed by Herbert Kahl, had arranged a very active day for everyone. The chief diversions were golf, swimming and tennis. The highly prized golf trophy was carried off by Robert Wilson, with Tom Larson runner up. The tennis singles prize was taken by John Hand, while the doubles match was won by William H. Cady and Norman D. Harvey, Jr.

The evening was terminated by a very excellent dinner, followed by a short business meeting. The meeting was brought to order by Chairman Heyward F. Lawton. The presentation of prizes was made by Herbert Kuhl. The following officers were elected for the coming year: Chairman, John G. Masson; Treasurer, Ben Verity; Secretary, Raymond A. Pingree; Councilor, Heyward F. Lawton; Members of Sectional Committee, Peter J. Ariente, Richard B. Earle, Richard Haworth and Philip C. Putnam. A motion was made and carried to the effect that a program committee be formed to take care of all arrangements for future meetings. Members of this committee are to be appointed by the chairman.

The meeting was adjourned at approximately 10:30 P. M. Respectfully submitted, RAYMOND A. PINGREE, *Secretary.*

APRIL MEETING, NEW YORK SECTION

THE April meeting of the New York Local Section of the American Association of Textile Chemists and Colorists convened in the Chemists Club, New York City, on April 27, 1934. Mr. Henry F. Herrmann, Chairman of the Section, presiding.

. . . Preceding the technical program, a business meeting was held. . . .

Chairman Herrmann: Gentlemen, we are privileged tonight to hear from a research chemist. Research has always appealed to me. I am sure it has a general appeal to all. These gentlemen are like the astronomers searching the skies for new things in a realm that, to us, is clothed in mystery. And so we are particularly fortunate to have with us tonight Mr. Arthur R. Murphy of the Dyestuff Manufacturing Department of the duPont organization, who is going to talk to us about the Azo Dye Research Chemist, and I suppose he is going to touch somewhat upon the research chemist's problems in azo dyes. Mr. Murphy! (Applause)

. . . Mr. Murphy then presented his prepared address. . . . (Applause)

Proceedings of the American Association of Textile Chemists and Colorists

Research in Azo Dyestuffs* and the Work of the Azo Dye Research Chemist

By **A. R. MURPHY**
E. I. du Pont de Nemours & Co.

IT is a pleasure to have the opportunity of discussing Azo Colors with the actual consumers and distributors. We, as research men, have little direct contact with you who control the destinies of our "brain children". The Sales Division acts as a "go between" and, since the customer is always right, your complaints and requirements are our troubles.

You present your story to the salesman, who in turn impresses us with it signfiicance. We usually give him some theoretical reason why you are wrong but, since theory doesn't sell dyes, we proceed to solve your problem.

I like to consider dye chemistry as I do medicine, which makes me an advocate of the specialistic idea. When I am ill it is a comfort to have a family physician who is an expert diagnostician so that in cases of emergency he will send me to the specialist who is the most capable of effecting a cure. The solving of dye problems is very similar. When you have trouble with your colors you do not call in a food chemist or an oil chemist; you desire a man who is an expert or a specialist in the particular field of dyes concerned. This is the man with whom I wish to acquaint you this evening, the Azo Research Chemist.

The Azo Color research chemist gains a large portion of his knowledge of Azo Colors in the industry. Very little azo chemistry is taught in our educational institutions. Of course, organic chemistry teaches the fundamental principles involved in azo chemistry, but these are surprisingly few. The preparation of an azo dye requires but two distinct organic reactions, diazotization and coupling (or development). These terms are familiar to practically everyone in the dye industry whether he be a manufacturer or a dyer, for these reactions are used not only in the manufacture of azo colors in substance but are also employed in certain dyeing processes to produce insoluble colors on the fiber.

Since the azo chemist's knowledge is gained not from text-books but by years of observation and experience, it will not be a surprise when I tell you that the average experience of the men in the azo research division of the du Pont Company is sixteen years.

You have been informed many times about the theoretical uncertainty of an explanation of light and washing fastness. Although there is some remarkable work being carried on both in this country and abroad, no definite acceptable theory is available to the azo man and yet without a thorough fundamental understanding of the involved principles he has developed fast colors and is constantly improving the properties of this valuable class of dyes.

We must not consider this as sort of a trial and error development or a hit-and-miss business for if we do we are underestimating the research man's reasoning power, for this and his experiences are his principle tools of success.

Without going too deeply into the chemistry of azo colors I would like to give you more or less of a sketchy picture of this interesting and absorbing study. It may be of special interest to you who have handled developed colors to see how complicated azo dyes are built up around the simple reactions of diazotization and coupling that you carry out every day in your dyehouse. It may also serve the purpose of describing the enormous field in which the research man labors and the future possibilities of improved types.

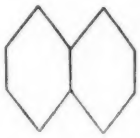
The origin of azo colors was explained to you by Dr. R. E. Rose, January 1932, in a discussion of "The History of Dyestuffs", and their manufacture was well described by Mr. P. H. Stott in his paper "A Short Discussion of the Manufacture of Some of the Better Known Dyestuffs" presented before this Society in December 1926. If you will pardon any repetition I will humbly

* Presented at meeting, New York Section, April 27, 1934.

carry on the thoughts which these gentlemen have previously presented.

Azo colors are built up around one or both of the coal tar distillation fractions

Benzene



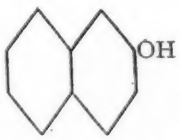
Naphthalene

which for convenience sake are symbolized as written. There are also a number of chemical groups which can be attached to these nuclei:

NH_2	OH	SO_3H	NO_2	CH_3	OCH_3
amino	hydroxyl	sulfonic Acid	nitro	methyl	methoxy etc.

These groups, when attached to the benzene or naphthalene nucleus, produce what we term dye intermediates, for example:

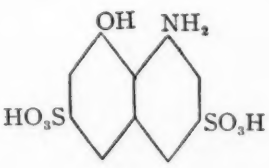
Aniline



Beta-naphthol

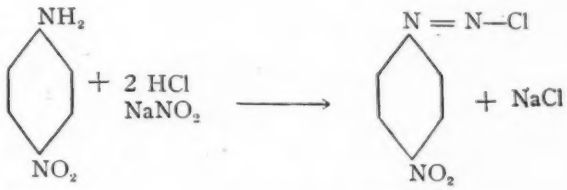
Para-nitro-aniline

Sulfanilic Acid



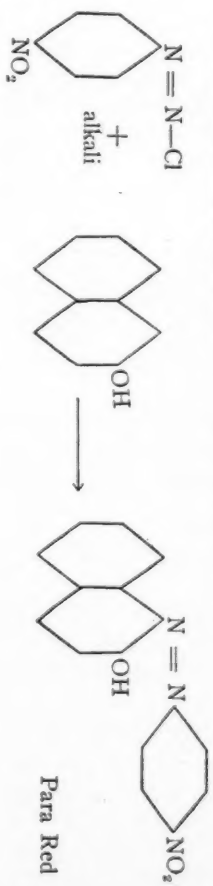
H-acid

If sodium nitrite is allowed to react with hydrochloric acid in a water medium, nitrous acid HNO^2 is produced; if this in turn reacts with an amino compound, diazotization takes place. This is best described as follows:



p-Nitrobenzene-diazonium chloride

These diazo bodies or diazonium chlorides have a strong affinity or attraction for other intermediates which contain amino or hydroxyl groups. When the two come in contact coupling takes place with the formation of an azo dye:



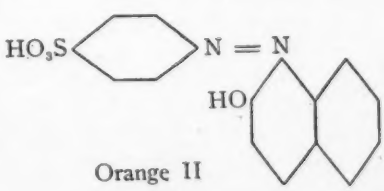
Para Red

Of course, this particular dye is insoluble and must be formed on the fiber to effect substantivity, but it illustrates the principle which is used in the manufacture of azo colors and describes the process which you use in producing developed dyes on the fiber. In developing diazo colors you are increasing the complexity of the original dye by adding additional azo groups and intermediates and simultaneously increasing washing fastness. The idea of building up azo colors is best illustrated by the fact that azo colors are divided into four main classes, dependent upon the number colors are divided into four main or azo groups in the dye molecule, monoazo, diazo, trisazo and tetrakisazo. These groups are in turn subdivided according to formation. For example:

Monoazo

(containing one azo group)

our old friend Para Red and:

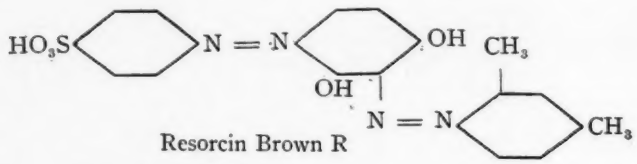


Orange II

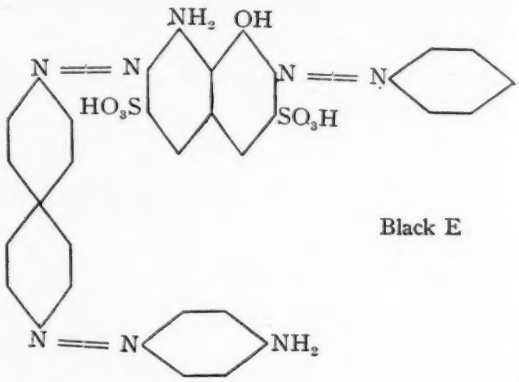
Disazo

The disazo colors, presenting more possibilities, are normally divided into four separate groups:

Primary Disazo:

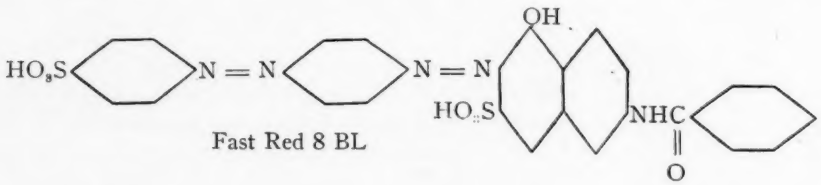


Resorcin Brown R



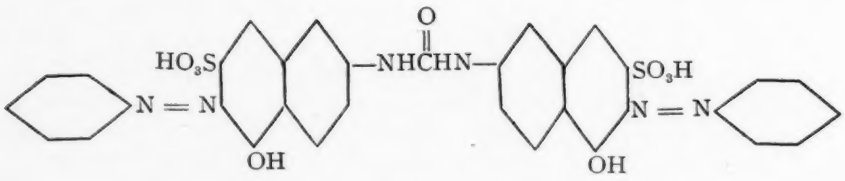
Black E

Secondary Disazo:



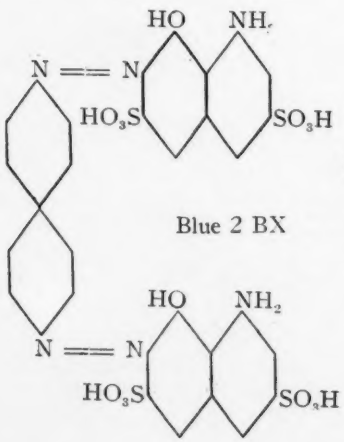
Fast Red 8 BL

Tertiary Disazo:



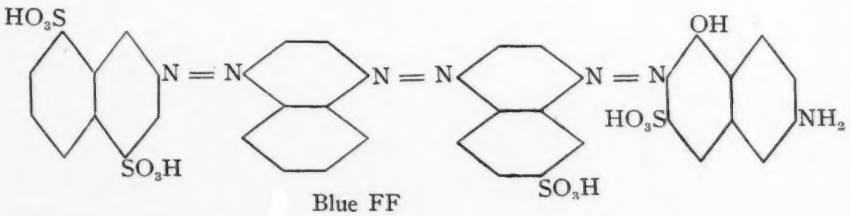
Fast Orange S

Disazo Colors Obtained from Diamines:



Blue 2 BX

The next type is represented by:

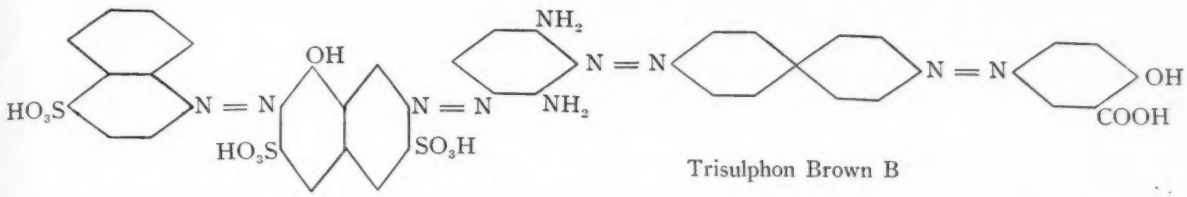


Blue FF

Trisazo

This class again becomes more complicated as the number of azo groups is increased to three and the possible combinations are much greater.

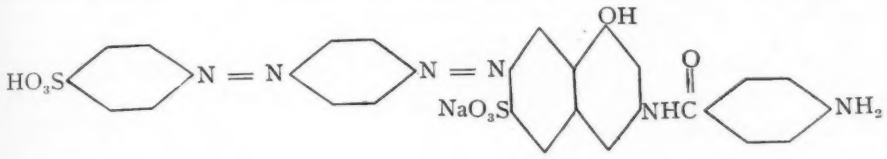
By far the most important color in this class is Black E: There are other types of trisazo colors which we will not attempt to consider at this time, but will present one example of a tetrakisazo to illustrate the possible complexity of azo dyes:



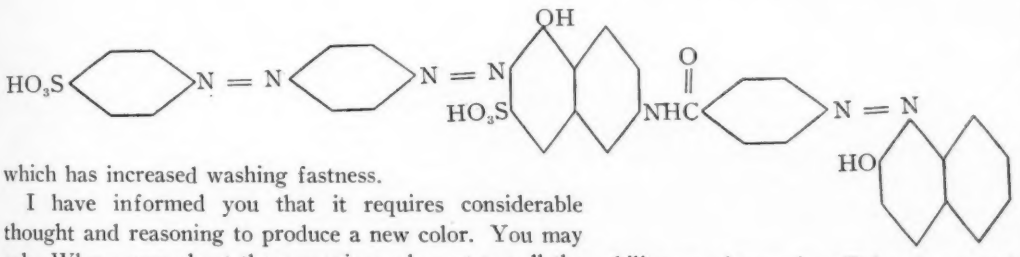
Trisulphon Brown B

This should give you some idea of the types of compounds the azo research chemist must deal with.

Before leaving this haze of molecules it might be interesting to draw the formula of a diazo type color with which you are all familiar, Diazo Red 7BL, and show the change in structure that takes place when this color is diazotized on the fiber and coupled with beta-naphthol.



The external amino group is transformed into a diazo group by treatment of the dyed fiber with hydrochloric acid and sodium nitrite; this, in turn, when developed with beta-naphthol, produces a trisazo color.



which has increased washing fastness.

I have informed you that it requires considerable thought and reasoning to produce a new color. You may ask: Why worry about the reasoning, why not try all the mathematical possible combinations, test the resultant products and have it over with? Let me show you that although this solution may be possible, it is not probable. A hurried glance through the Colour Index shows approximately 230 intermediates which are common in the preparation of azo colors. One hundred seventeen of these are capable of diazotization and can be considered as first components, while 142 are components which promote coupling. Now, if we calculate the mathematical possible combinations, we find that it is possible to form

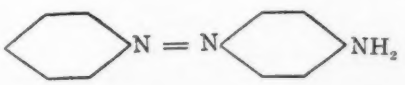
19,000	monoazo colors
960,000	primary disazo colors
281,000	secondary disazo colors
28,000	tertiary disazo colors
605,000	diazo colors from diamines
86,400	from disazo diamines acid coupled
1,979,400	or a total of

or approximately 2,000,000 possible monoazo and disazo colors from the 230 intermediates given in the Colour Index. When we start to consider the trisano colors we find in one type alone over 4,000,000 possible combinations. These figures compare with the chances one has of winning a lottery or a baseball pool. It must be remembered that we have not considered the many other types of trisazo colors and the entire class of tetrakisazo dyes. If we would and to these possibilities the many more special intermediates which are not mentioned in the Colour Index we would be competing with the astronomer in his calculation of distance.

If we realize that it costs approximately $500. to make complete property tests, we see why thought in azo research is a money saver.

The research man must know what combinations to try to give the desired effect, whether it is improved light fastness, washing fastness, change in shade, improved solubility or change in affinity for certain fibers. I have had prepared a few dyes which were built around the simple nucleus of aminoazobenzene. Let us consider these colors.

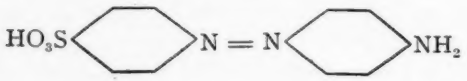
If we start with aminazobenzene



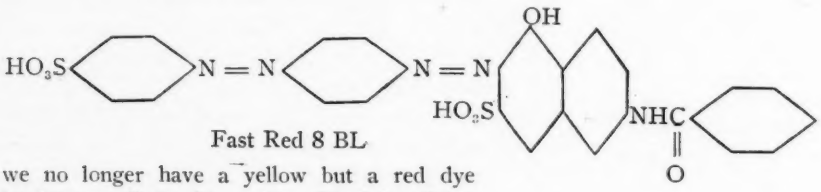
an insoluble dye which is only soluble in fats and other organic solvents, we must in some way effect dispersion to test its dyeing properties; this is most readily accomplished by dissolving the dye as the hydrochloride and precipitating with alkali in the dye-bath in the presence of soap. If we attempt to dye a union material consisting of acetate silk, silk, wool and cotton we find that only the acetate fibers are dyed and these very readily. Although this dye has enormous affinity for this definite fiber it, like

many other simple aminoazo bodies, cannot be considered a valuable acetate silk color due to its sensitivity to acid, storing, and light. It serves to illustrate our point of the effect of substituents on the dyeing properties of an azo color.

If we add a sulfonic acid group to this color so as to produce the following dye:



a distinct change in dyeing properties takes place; we no longer have an insoluble product but one readily soluble in water and find that this product does not dye acetate silk or cotton, but has definite affinity for silk and wool. If we go one step further and add another azo group and another intermediate, resulting in the following dye:



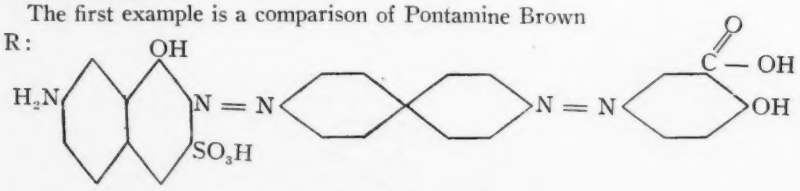
Fast Red 8 BL

we no longer have a yellow but a red dye having no affinity for acetate silk, fair affinity for silk and wool, and good affinity for cotton.

I have had dyeings prepared to show these definite changes.

Before leaving this point of the effect of constitution on the properties of dyes I would like to show you two examples of isomeric dyes, that is, dyes of equal molecular weight and containing like intermediates and identical substituents which, due to arrangement of the substituents in the molecule, exhibit entirely different characteristics.

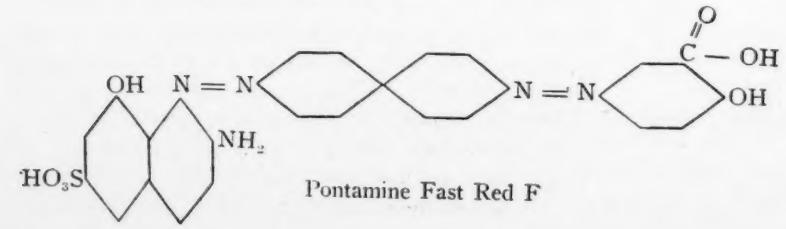
The first example is a comparison of Pontamine Brown R:



Pontamine Brown R

and

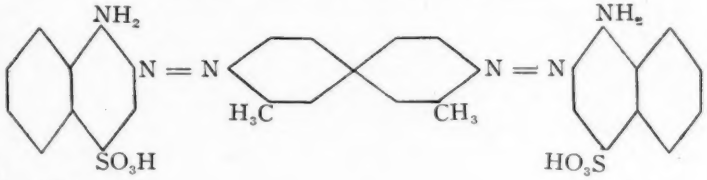
Pontamine Fast Red F



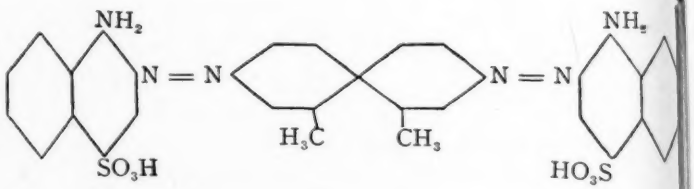
Pontamine Fast Red F

By changing the coupling position of the Gamma acid we have changed the shade of the dye from a brown to a red and have effected a distinct improvement in light stability.

The second example, although time-worn, is still a classical illustration of the point under consideration. Purpurine 4B which is prepared by coupling tetrazatised tolidine to two moles of sodium naphthionate:



is a red dye having good affinity for cotton and poor affinity for wool. If a simple change is made in this molecule, that is, the use of the isomeric toludine to form:



we obtain an orange dye which is valueless as a cotton color but possesses good affinity for wool.

I have shown the enormous change in property of an azo color that can be brought about by a simple change in constitution. These are little "tricks" the research man uses every day and are only gained by constant observation, reasoning, and experience.

Another very important factor in the education of the research man is a thorough knowledge of the patents concerning the branch of work in which he is interested.

In the case of the dye chemist this is not only a source of information as to the advances being made by competitors, but it also is a very important factor when consideration is being given to experimental work and to the final marketing of a new color. An enormous waste of time and money results from lack of patent consideration.

We may have spent considerable time qualifying the research man, but it is my purpose to interest you in his work so that through cooperation between you, the gentlemen who discover new uses for dyes, and the men who produce these colors the dye field will continue to advance to a greater degree than we may all realize.

It may be interesting to follow a few of the problems that are presented by the trade to the research man:

A demand has arisen in recent years for colors of improved discharge properties. I believe this is especially true in rayon dyeing and discharge printing. For a long time the research man "got by" by telling the salesman that poor discharge was solely an inherent property of the dye in question. This was all right until he went back and tried to sell the idea to the customer. Perhaps the first time he came around the customer accepted the idea because an "inherent property" sounds rather scientific and in this day and age we all like scientific explanations. But the second time the salesman called the customer said: "Say, about this inherent property business, why doesn't "Calcinol Geniline's" dye which is identical in shade and fastness properties to your color have a poor discharge?" Well, you can see where the poor research man stood. There is a popular expression which adequately describes his position. He stood on the old proverbial "spot". What happened then? He got busy, forgot his theory and found that perhaps he wasn't 100 per cent correct after all. There was something in the manufacturing process and quality of intermediates which, when improved, resulted in a higher quality product more useful to you—and let us say, an advance in the art of dye manufacture. Just a passing word to the research man: In some colors this "inherent property" is still the best alibi, for there were some colors that could not be improved by change in process or quality of intermediate. It became necessary to change the constitution of the color to effect improved discharge. This was not an easy task for in most cases the customer demanded similar shade and fastness properties.

Solubility is another favorite complaint. Much work has been carried on to improve the solubility of certain colors. This improvement in many cases has necessitated an expensive change in process and an accurate control of the hardness of the processing water. I am afraid many scientists would question our method of describing the solubilities of certain dyes when we say that they are soluble in Passaic water but insoluble in Chicago water. What we mean is that the dye dissolves in water with a hardness of approximately 35 parts per million but precipitates in water with a hardness of 125 parts per million. The question of solubility of dyes is not always a question of true solubility but is a question of its lack of ability to form insoluble lakes with the calcium, magnesium, iron, etc. in the water.

An interesting example of the true solubility principle is its effect on the cold beater method of dyeing paper. This method consists in adding the dry dye to the pulp, alum and sizing in the beater. A certain dye found satisfactory by laboratory tests gave equally satisfactory results in the mill in summer but when used in the winter complaints were received as to the strength of the product. Investigation showed that in this mill the water was never over 35°F. in the winter. Now, if you have ever tried to dissolve color in ice water, you appreciate the problem that was presented. But as I reminded you earlier the customer is always right. So the research man was put to work to solve the impossible, to improve the solubility of a definite organic compound. To some this may sound as possible as raising the melting point of a pure organic compound, but please consider that in speaking of solubility I am referring to apparent solubility which to the dyer is as effective as true solubility.

A third problem which is frequently presented is the improvement in washing fastness. We all agree that washing fastness is directly connected with affinity or substantivity. This substantivity is in some way related to the structure of the molecule, but further than this we have not the theoretical background to obtain, without considerable experience and experimentation, improved washing fastness. There may be a time, let us hope in the near future, when we will solve this problem of substantivity and with this knowledge develop new direct dyeing colors of extreme fastness.

At the present time the research man depends on his store of experience and observation to give the dyer colors of improved fastness properties. Since experience teaches that there are many factors which influence this property of washing fastness, it becomes necessary to combine these factors to the best advantage.

I have attempted to present to you this evening a picture of the azo research chemist, the field of unlimited possibilities within which he labors, the problems with which he is confronted, and to show how his interests are controlled by the dyers' problems.

It is difficult to thoroughly present a subject as broad as azo colors but it is only through a better understanding of the dyers' problems by the dye chemist and an appreciation by the dyer of the research man's endeavor to cooperate that advances can be made in the art in which you and I have dedicated our efforts.

Discussion

Chairman Herrmann: I thank you, Mr. Murphy.

I hope I am not presuming on Mr. Murphy's kindness in inviting the section to discuss his paper and to ask him some questions. Will you receive them?

Mr. Murphy: With pleasure.

Chairman Herrmann: Thank you.

It has been my experience that papers of this type are not discussed as freely as they should be, not because they are not so interesting but because some of us may be a little reluctant to cross swords with the expert; but surely there is plenty of material here to stimulate the interest and imagination, and if you have any questions I am sure Mr. Murphy would like to have them.

Mr. Murphy: I would like to say that the research man is looking for ideas from the consumer. It is only through these ideas and through the presentation of your problems that we can hope to improve the dyes as a class. So we are glad to receive any suggestions you may have.

Chairman Herrmann: I would like to ask Mr. Murphy by way of starting—this is probably purely conjecture—what the likelihood is that the 85,000 possible combinations and permutations of the known intermediates listed in the color index have ever been assembled into dyes and ever tried out and found wanting, and to what extent one might consider that those dyes which are today commercially active are the only ones existing in that group which have such properties, or whether the research chemist is today still looking among these combinations for products which may tomorrow be of commercial importance?

Mr. Murphy: To answer that, Mr. Chairman, I would say that not all of the combinations have been tried, and will not be tried due to the fact that experience has taught the azo man that there are some combinations which would be foolhardy to attempt. In the first place, experience has taught that the desired properties would not be inherent in the final color and then we must consider the physical impossibility of making some of these combinations.

The big field in new azo colors and in new combinations lies in the development of new intermediates. I think, from the few examples which I have given this evening and from the number of possible combinations I have shown can be obtained from the 230 existing intermediates, that the development of one new intermediate usually opens up a very vast and large field of experimentation.

Chairman Herrmann: From which we may conclude that it is quite unlikely that some very simple combination is apt to be discovered, that what is coming now will probably be more and more complex, because we are adding and adding and adding groups, the same as you were filling the blackboard.

Mr. Murphy: I would hate to commit myself on that because in the last couple of years we have gone back to some of the old simple, cheap colors, and maybe we have been "railroaded" into this idea of having complex colors, when the simple colors would answer the purpose.

Chairman Herrmann: The same as the person who invented knee action in the automobile industry and found that the car of 110-inch wheel-base is as good as the car of 150-inch wheel-base.

Mr. Gilchrist: I wonder if Mr. Murphy could give us some generalization of what the different groupings add to the properties? As I understand it, sulfonation adds solubility, and I wonder what nitration or acylation or any of the other groups add to properties? If you could give us some general idea of what the different additions give, it would be helpful.

Mr. Murphy: That is a very reasonable question. Acylation of hydroxyl groups usually affects alkali stability, improved fastness to alkali. The addition of sulfonic acid groups to the molecule in all cases, of course, affects solubility, but the addition of a number of such groups has a tendency to decrease the cotton affinity and increase the wool affinity, resulting in a more acid color. You see, the addition of the sulfonic groups adds to the acidity of the dye molecule, which in turn gives us our acid colors.

Other negative substituents as nitro bodies—also have the effect of lending acidity to the dye molecule and making it an acid color. Nitro groups very seldom increase the substantivity of a dye for cotton.

There has been considerable conjecture as to the position of the sulfonic acid group in the molecule—and its effect on the light fastness of the color. There is considerable in the literature to show that a sulfonic acid group placed in ortho-position to the azo group improves light fastness.

The methyl groups and methoxy groups, which we didn't mention, tend to deepen the shade of the dye. The number of azo groups in the molecule, if placed in a position para to each other, also deepen the shade of the color.

Chairman Herrmann: Did you have a question, Doctor?

Dr. Bren: Mr. Chairman, let's take the hypothetical dye, and as a consumer we will buy it and it is in a particular physical form and on adding it to a product will get a definite undertone or overtone, or we may get a particular heat fastness or a light fastness. Along comes the salesman and he says, "We have improved the strength of it; it is now double X concentrated." It is the same color, but concentrated. We find that the undertone is changed even though we take the original color, get its

depth the same, and we find that the undertone or the overtone is changed, the heat fastness is changed or the light fastness.

How could the physical property change? I meant to ask that of Dr. Rose or Dr. Martone.

Mr. Murphy: I do not quite understand what you mean by the "undertone" of a textile color.

Dr. Bren: For instance, you get a red, and sometimes you get a shade depending upon the light, particular light. You may get a different overtone in one case or you may get a different undertone. That is especially if you use it with pigments. Our problem is just a little bit different from the ordinary adsorption of colors in textiles, but I think it refers to it in the same way.

Mr. Murphy: The only way I could explain the phenomenon, you point out, would be to say that you have not as much dye on the fiber in one case as you have in the other. Do you get equal strengths? Are you dyeing to an equal strength basis?

Dr. Bren: We add a definite color. We don't actually dye. We add that amount of color, see, and therefore I think that our problem is really simpler than the dye man where it is a case of adsorption, and yet when we match for depth and strength and compare the samples, we get an entirely different shade and yet it is the same color supposedly. We have had three examples, haven't we, Wilkins?

Mr. Wilkins: Yes.

Dr. Bren (continuing): Where in the one case there was a change of color; another case was heat, and third was light fastness. Supposedly the same color except concentrated.

Mr. Murphy: It is difficult for me to realize the situation, because a definite dye is a true definite chemical compound, and if you have the same amount or an equivalent of color on the fiber in both cases, you should have the same tinctorial effects whether overtone or undertone.

I realize that when you are considering overtone and undertone you may be talking from a lake man's point of view; but from the textile man's point of view, if we have an equivalent amount of color on the fiber, we must remember that we have the same definite chemical compound on that fiber, and we should get the same effect. You may have an entirely different story here than a textile man has.

Let us go back to this question you brought up about our salesman coming around and telling you that he has an improved type, that it is stronger than the other type. There is more to this than we sometimes realize. He has not always gone ahead and given you just a concentrated product; that is, left out half of the diluent which you normally might have received. He may have given you a product which has improved exhausting properties, improved affinity for the fiber, a dye that is stronger in comparison to its true organic content. It is normally considered that impurities in the dye hinder the exhausting properties of the color. A small amount of impurities will give an exhausting property to the dye which is much inferior to that which you would normally expect. Due to improved intermediates you may be receiving a dye of higher purity which exhausts more rapidly and more completely than the former product.

Mr. Wilkins: In the azo colors, what generalizations can be made, if any, of the effect of the different groupings and molecular configurations upon the reduction potential of the dye?

Mr. Murphy: You are, I think, hinging a little on the discharge problem. Outside of that I haven't much to say concerning the reduction potential of azo colors. I have had very little experience in relation to the true reduction potential of azo colors. Although we reduce many colors, we are chiefly interested in reductions with titanous chloride and discharging with hydrosulfide.

There are certain groupings in azo colors which seem to result in incomplete discharges. This is a big problem with all dye manufacturers. As I think I pointed out, this may be due to impure intermediates, or is just an inherent property of the dye. We have no theoretical explanation of the failure of an azo dye to completely discharge. Although they all discharge to a degree, there are some that fail to discharge to a pure white.

Mr. Wilkins: When you do have available the time required to discharge a dye, wouldn't that be proportional perhaps?

Mr. Murphy: I think in some cases that may be directly connected to the insolubility of the color. I have observed —this is really more or less of a personal observation— that soluble colors seem to reduce more readily. This, of course, can be accounted for by the fact that it is more completely in solution and more completely exposed to the reduction medium. Insoluble colors—para red, the example I have given tonight—is rather difficult to discharge in a water medium, due to poor solubility. I think that solubility may have an enormous effect on the discharge or the reduction properties of a color.

Question: Is there any direct relationship between the amount of impurities in the intermediate and its effect on the discharging qualities of the dyestuff?

Mr. Murphy: You are sure you are not going to hang that on the salesman?

Question: No, as a matter of information.

Mr. Murphy: As I said, in some cases, yes. The discharge properties of the dyes have been improved by improvement in the quality of the intermediates, but that is not the whole story. There are some azo colors which have this inherent property and for which this is our only alibi.

Chairman Herrmann: I don't know whether I should venture an opinion upon the problem that the Doctor here propounded before, and that is on the variation of top tone and undertone, apparent strength of some colors that, I imagine, belong rather to the insoluble group, but I think every lake man's experience has been that such a simple combination as para-nitro-aniline and beta-naphthol —and I will go so far as to say that if you were to offer a panful of the coupled color and distribute it to five different men and tell them to filter it and dry it each according to his own method, that you would get five separate and individual products because of the possible difference in the filtering, in the pressing, in the temperature of the drying.

I think all of us agree that the temperature of drying has a tremendous influence on the physical form, the softness, the impalpability of the powder, and that after all is a physical condition that contributes so very much toward the pigment value of a product. I had not so very long ago a very startling experience which, nevertheless, is a common occurrence with men who work with pigments continually.

We had a given product and the customer criticized it as not being fine enough. So we had it ground finer and found that we lost about thirty per cent of its tinctorial value in grinding. We gave it to somebody else to grind. He ground it to the same mesh with a different piece of apparatus and increased the strength thirty per cent.

That seems almost impossible, but it is gospel truth—that the type of grinding, whether it be a cleaving, a shattering, a wiping, creates particles of different shape, different size. They either present flat surfaces or sharp, acute points. The difference between crystalline and amorphous products has a tremendous bearing on the tinctorial value of insoluble products.

Dr. Bren: I know that is the case with insoluble products, but this problem that we have noticed has been with soluble colors, say. They may be lakes in some cases, but actually dissolve in the medium.

Chairman Herrmann: Are they solutions or just dispersed?

Dr. Bren: I believe, on account of the transparency, that they are true solutions. They must be true solutions on account of the transparency. They can't be fine dispersions.

Mr. Daniel J. Graziano: I wanted to ask Mr. Murphy a question regarding identification of dye. Specifically where you have a direct and diazotized dye specified, what positive tests would you give for identifying that? That is, what positive tests would tell you whether it is direct dye and what part of the test whether it is diazotized dye?

Mr. Murphy: I would say just put it to practice. Diazotize and develop it. Normally diazo colors change shade and have improved washing fastness. The gentleman asked how to identify a diazotizable or developed color.

Mr. Graziano: I have in mind on a finished product on a given textile.

Mr. Murphy: The same test holds true there. I would diazotize it on the fiber, couple to beta-naphthol, and test the washing fastness before and after development. The washing fastness of a diazo color normally improves by diazotization and development. Also, it is very seldom that you have a diazo color that does not change shade on development because, as I pointed out before this evening, on development you are adding another azo group and another intermediate which builds up the molecule, and results in a change in properties, and usually a change in shade.

Does this answer the question? Have you tried this method of identification?

Mr. Graziano: The usual methods that I have tried in the laboratory are the stripping methods, using chlorid or titanium chlorid. That is more of a group test.

Mr. Murphy: There are many diazo colors which strip, reduce, or discharge just as readily as the direct colors and just as completely. A developed color is still a dischargeable color.

Mr. Gilchrist: Mr. Murphy, in regard to that, the number of colors that despite the fact that they are not developed may be developed, and just because you can diazotize and develop, and you notice an improved washing fastness, they do not fall in the developed class. Is there any other method surer than the one of which you have just spoken?

Mr. Murphy: No, I do not think so. I think this is the best method. Maybe I do not get your point. You want to identify a dye on the fiber, and you want to distinguish between a developed color and a direct color. Many developed colors are direct colors. They can be used as direct colors if you wish to accept their shade and fastness properties; but the difference between the developed color and the direct color is that the developed color has a free external amino group which is capable of being diazotized and coupled. When you apply this reaction to the dye on the fiber, and if it is a true diazo color, you change the property of the dye, because you are building up the molecule. You are increasing the molecular weight and decreasing the solubility of the color on the fiber, which results in increased washing fastness. Since you are adding azo groups and an additional intermediate (beta-naphthol), you are normally changing the shade of the color. The perfect developed color would be the color that would not change shade on development.

Mr. Gilchrist: Would not a surer method be of reduction and testing for bleeding? An undeveloped color would bleed more surely than the developed?

Mr. Murphy: Not after reduction. It would on the

fiber before reduction. I previously said a washing fastness test would be one of the tests, but reduction of the color on the fiber should in no way distinguish between a developed and a direct color. A good developed color does reduce and discharge. There are a few that do not, like a few direct colors, but this should not be a positive test. The rate of discharge on the fiber really is not a positive test to distinguish between a developed and a straight substantive color.

I think the method of diazotization and development and testing the washing fastness before and after development will in most cases indicate whether or not you have a direct or developed color.

Mr. Zilessen: Let us take, for example, two cases, one where you have a select, direct dye, of good fastness, and another case where you have a developed dye. You are making a test such as you describe for developing it further, and you may have a developed color, as I pointed out in the second case, where you wouldn't get any increase or change in shade as you would if you tried to develop on top of the development.

Let's say in the other case you have a direct dye and you don't get any change either, how are you going to be sure not knowing beforehand whether you have a truly developed dye?

Mr. Murphy: I am sorry I didn't get that point. You have two pieces of goods that are dyed with two separate colors, yours and your competitor s, and you want to find out whether or not he is using a developed color to match your direct color. That is an entirely different question.

Mr. Zilessen: That is the point that some of the previous gentlemen tried to stress. Is there any way that you can still be sure that you have a direct dye there?

Mr. Murphy: No, and I do not think the question of reduction would be a true test to differentiate between the developed and the straight color because, as I said before, developed colors reduce and discharge in most cases just as readily.

Mr. Zilessen: In that case there would not be a positive test.

Mr. Murphy: Not that I know of.

Chairman Herrmann: There is only one bit of comfort for the chemists there. If the shade is not particularly fast to washing and if it had been dyed with a developed color, it would not be a very good one. So if it is reasonably fast to washing, I suppose one could almost assume that it was a developed color, and if it is not fast to washing, the presumption is that it is either a direct color or if it was developed it wouldn't do it much good.

Mr. Zilessen: Isn't it true that it is possible to have a certain developed color, not developed for fastness but developed for color?

Chairman Herrmann: They are the oddities, they are the exceptions.

Mr. Murphy: They are the exceptions.

Chairman Herrmann: Those developed colors which are not as good as direct colors really have very little excuse for existing.

Mr. Graziano: I have found that where some colors have a free amino group, when they are diazotized and developed, their brightness is improved, whereas their washing fastness has not been improved. I have also found—I may be wrong in this idea, but from some experience I have had when diazotizing and developing the ordinary direct colors which have no free amino groups—that they become much duller in shade and somewhat weaker, and their fastness is not improved; whereas, the developed colors when diazotized and developed, their brightness and their fastness is improved.

I would say from my experience that the developed colors improve in their brightness in some cases and in a number of cases their fastness in diazotizing and developing, whereas the ordinary direct colors which have no free amino groups become duller in their diazotization and development.

Mr. Murphy: That is right. I would check your observations because a number of our ordinary direct colors not only are not capable of being diazotized but they have groups similar to this group here, which I think is a rather good illustration of ortho-amino groups. The diazo color has an amino group para to the azo group, whereas many of our direct colors have amino groups ortho to the azo groups; and nitrous acid has an effect on this grouping which tends to dull the shade. This is very noticeable in a good many of our direct colors, whereas in a true developed color, the free amino group is normally in a para position to the azo group are in some way blocked from the molecule, allowing true diazotization.

I do not know how to illustrate this blacking effect, but I think Diazo Red 7BL, where the amino grouping is entirely blocked from the rest of the molecule by a benzoyl nucleus is a good illustration. In a color similar to Purpurine 4B, I would predict a dulling effect upon diazotization.

Chairman Herrmann: I believe, when you diazotize ordinary blue, 2b, 3b, you get that peculiar grain.

Mr. Murphy: That is right.

Chairman Herrmann: Gentlemen, if there is nothing further to come before the Section, I would like to call for a rising vote of thanks to the speaker, Mr. Murphy, as wall as for the Program Committee.

. . . The members arose and applauded. The meeting then adjourned . . .

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—H. C. Chapin, Secretary, Lowell Textile Institute, Lowell, Mass.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

Note. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the American Dyestuff Reporter.

A-2

Education—B.T.C., Lowell Textile Institute, 1932; also course in typing.

Experience—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, woman, single.

A-5

Education—B.T.C., Lowell Textile Institute.

Experience—Assistant chemist in carpet mill, dye tester in dye plant, research and analytical work in silk dyeing and finishing plant laboratory, plant chemist and overseer of bleaching in surgical dressing plant, assistant chemist in woolen mill. Age 29. Married.

A-6

Education—Analytical chemistry and dyeing course at Lowell Evening Textile School.

Experience—Three years as print chemist and one year as dye chemist for large print works. Two and one-half years as plant chemist for dyeing, bleaching, printing and finishing plant.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-C-1

Education—Graduate Industrial Chemical Engineer, Pratt Institute—1911.

Experience—One year as plant control chemist, 4 years as laboratory chemist with gas company, 13 years as plant chemist with bleaching, dyeing and finishing plant. (Rayon and cotton piece goods). Formulated processes and put them into plant operation, 1 year as chemist and demonstrator for dyestuff company, 1 year as superintendent colorist with print works printing linen and rayon, 1 year as director of testing laboratory for national dry goods concern.

A-E-2

Education—B.T.C., Lowell Textile Institute, 1933.

Experience—Assistant instructor in chemistry, Lowell Textile Institute. Member of scholastic honorary fraternity.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-12

Education—2 years days at N. Y. U. and 3 years nights studying chemical engineering.

Experience—1½ years asst. colorist, 5½ years colorist. Experienced on vats, commercial and fast colors on cotton and cotton-rayon mixtures. References; age 29; married.

B-13

Experience—Large experience as an assistant colorist chemist in silk printing, dyeing and finishing; also on cotton and wool dyeing. References.

B-14

Education—Rhode Island School of Design.

Experience—Familiar with all classes of wool dyeing. Seven years with large carpet mill as dyer and processor of washed oriental rugs. Will go anywhere, married, 37 years old. References.

B-15

Education—B.T.C., Lowell Textile Institute, 1934.

Experience—Experience in dye house running washers, dye kettles and as a dye weighter.

F-1

Education—Textile Institute, Alexander Hamilton Inst., Extension work at Brown Univ., working knowledge of German.

Experience—Has had executive departmental work with all types of textiles manufacturers. Acquainted with all types of textile machinery, dyestuff application, laboratory practice, cost methods, and checking methods and processes. References.

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INTEREST IN GOVERNMENT

HINTING that the caliber and opinions of the next Congress are quite as important to the American business man as is the development of his next sales program, Henry H. Heimann, executive manager of the National Association of Credit Men, has urged the 25,000 members of that organization to "get into more active participation in governmental affairs." He urged the members of his association, who direct the credit and financial affairs of the larger wholesale and industrial institutons, to see to it that efficient candidates are put up for office.

"Learn all about your candidates," Heimann said in his message to his members urging active participation in politics. "Learn their views on money, on labor, on business, on profits, on legality of contracts, on sense of obligations. See that they declare themselves and then help organize business so that it can politically express itself."

The Executive Manager of the National Credit organization, who until recently served as Director of the U. S. Shipping Bureau, made it quite plain that business had only itself to blame if the actions of the next Congress were not suitable. "At no time in recent years has it been so essential that business men become actively interested in government," Heimann continued. "Instead of railing against politicians, they must be politicians in the sense that they must help mould public opinion and do their utmost in seeing that good men are put into office. It is as vital to business to have a good, efficient Congress these days as it is for business to have good banking connections.

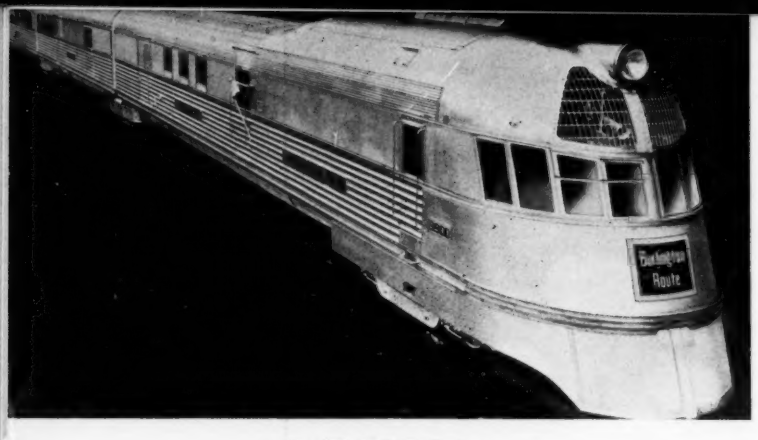
"If business men say politics is all wrong and they will have none of it, they are worse than an ostrich that seeks safety of body by hiding its head in the sand. Their business lives are more closely linked with government operation than at any other time.

"I do not mean, necessarily, that business men should aspire to office, though some should make the sacrifice. I mean they should get into action and see that efficient candidates are put up for office. It may be as essential as a sales program. It may be as vital as the capitalization of their companies.

"If business men hold themselves aloof and feel superior to politics then they can expect the kind of politics of which they have so frequently and vehemently complained. It would be well to pause and consider whether our politics in this nation is not the direct result of this past indifference towards government by business men. In my opinion the greatest contribution business men could make towards business and government would be a more active interest in government."

Indicating that a fear of inflation is still holding back business progress, Heimann pointed out that a growing sentiment prevails, even among many strong supporters of the administration, that the monetary policies pursued have not been beneficial. "Such fear as exists today is not so much concerned with what has been done as in regard to what may be done in the future. With our public expenditures and debt mounting and with the certainty that they will continue to mount, there is rapidly increased feeling that some form of additional inflation—either money or credit or both—is almost inevitable. It is difficult in times of such uncertainty as now exist, to formulate and adhere to rigid policies—for new emergencies may make it mandatory to change policies to meet new situations. However, just as it is true in our labor situation that a greater clarification of policy would be of tremendous advantage, so it is true that greater assurance regarding at least the objectives to be sought in our policies concerning money would be helpful in engendering the confidence necessary to an easier flow of capital."

"Some of the recent trends in modification of the NRA program, while comparatively slight in themselves, are of importance as probable indicators of future trends," Heimann continued. "I refer to such steps as the recession from the earlier policies on price fixing, and the service industry codes. Aside from the importance of these steps in themselves, they have a broader aspect as indicating a recognition of the utter impracticability of the federal government administering all business affairs. From time to time, further recessions will undoubtedly be made. We still believe in this country that there are economic laws which cannot be permanently displaced by statutory enactment. * * *"



The "Zephyr"—Burlington

Textile Fibers in Thermal Insulation

By **HERMAN BOXSER**
Chicago, Illinois

ONE of the aims of modern science has been to make the human race as comfortable as possible. It has perfected many ideal heat distributing mechanisms which produce comfort from the elements of cold during the winter. At present great studies are being made for perfecting units wwhich will provide greater comforts in the home during the hot summer months by air cooling and conditioning.

Comfort has not only been sought for by the technician in the home, but also in our transportation systems—in the automobile and in the railroad car. In the planning of the automobile body, the proper insulation against drafts and cold air seepages has been a vital angle considered by the automotive engineer.

The refrigerated railroad car with its complete insulation has made possible the transportation of perishable foods over great distances, with the assurance that these foods will reach their destination in excellent edible condition for the table.

Of particular interest at this time is the role to be played by textile fibers in new changes being evolved in our railroad transportation systems. Reference is made to the new lightweight cars developed by the Burlington & Union Pacific Roads. In these cars experimental work had been executed with materials made from textile fibers, although mineral fibers were finally selected. As shown in the small figure on the next page the insulation in a railroad car is applied in the aperture between the outside and inside walls of the car.

In the development of these transportation systems proper heat insulation has been a prime factor. Of what importance have textile fibers been as heat insulation? In the following, the writer will attempt to briefly describe insulation, its measurement, and to offer a description of insulating materials containing various textile fibers.

Heat Insulation and Its Measurement

Materials which are poor conductors of heat are heat insulators. Metals are better heat conductors than non-metals. In general, gases are the poorest conductors of heat, but other factors such as convection, alter these properties. Gases, such as air, confined in a fibrous substance, such as a textile material lend excellent insulating properties to the latter.

Commercial insulators may be divided into two general groups:

(1). Fibrous materials either loose or fabricated into soft quilts between thin layers of paper or a woven textile.

Table I

Fiber	*Density in lbs. per cu. ft.*	*Thermal conductivity in B.t.u. per hr.*	*Authority*
Cotton	3.3	0.239	Bur. of Standards
Pure Wool	4.99	.260	Bur. of Standards
Silk Noils	0.9	0.256	.....
Kapok	1.0	.240	Bur. of Standards
Jute	9.0	.274	Bur. of Standards
Flax	2.4	.269	Bur. of Standards
Sisal	6.8	.267	Bur. of Standards
Curled Hair	3.6	.374	Bur. of Standards
Cattle Hair	13.0	.260	Bur. of Standards

(2). Rigid boards in which the components are bonded together either by pressure or with an adhesive.

The majority of textile fibers utilized as insulators fall under group I, although cellulose is often used as a base for insulators in group 2.

Insulation is measured in terms of thermal conductivity which is the numerical measure of the ability of a substance to conduct heat. It may be defined as the amount of heat measured in B.T.U. (A B.t.u. equals the amount of heat necessary to raise the temperature of one pound of water one degree Fahrenheit) which will flow in one hour through a uniform layer of material one square foot in area and one inch in thickness, when the temperature difference between the surfaces of the layer is maintained at one degree Fahrenheit. A material which will allow the least amount of heat measured in B.t.u. to flow through it will be the best insulator. Thus the lower the numerical value or thermal conductivity the better the insulator.

A much used method for testing insulating materials

is the Plate Method. This has been in use for a number of years by the United States Bureau of Standards. This method depends on the maintenance of a constant temperature difference between two flat metal plates mounted parallel to each other, and measuring the rate of flow through a flat slab of test material placed between the plates. The test material is kept in good thermal contact with the plates by means of pressure with the results that the temperatures of the plates are the same as those of the surfaces of the insulating materials in contact with them. The thermal conductivity is then calculated according to the definition which we have previously described. Insulating materials possessing the thermal conductivities of from .25 to .30 B.t.u. per hour may be considered in the class of good insulators.

Table I gives the thermal conductivities of the principal textile fibers. Rayons are not included in this table since the writer knows of no commercial insulating product which contains these fibers nor is he aware of any authoritative thermal conductivity tests which have been conducted for this class of fibers.

It is interesting to note that the insulating properties of fibers will vary under varied conditions of temperature as well as with their purity. Thus fibers in a bone dry condition will show a lesser thermal conductivity than a conditioned fiber.

Wool in the grease will act as a poorer insulator than a pure grease free wool. Tests conducted on pure silk as compared to scrap taken from a spinning mill showed the former to be the better insulator.

Chamberlan & Speakman (Jour. Text. Inst. 21, T39, 1930) in studying the thermal conductivity of textile materials noted that increased milling had the tendency to decrease conductivity of heat through materials. This would bear out the tests which show that the purer the fiber the less it will conduct heat.

In the development of commercial insulators, fibers of the least weight and density, as well as those which are cheapest, have been selected. For this reason the major fibers used commercially in the insulation field are (1) Jute (2) Cattle Hair (3) Kapok (4) Flax. Cotton, wool and silk are out of th eprice range of cheaper raw materials.

Kapok has excellent heat insulating properties and is the principal component of one of the best known commercial insulating materials. However, due to its greater expense, a commercial product results which costs more than the average run of insulators. A second drawback lies in its greater tendency towards inflammability.

Mention has been made by Chamberlain (Soc. of Chem. Ind. Jour. 51, 89T, 1932) of the possibility that wool should provide an ideal insulating material for use in small heat storage and refrigeration apparatus. He states that:

"The material has definite advantage over cork and asbestos in that it does not develop cavities with time and has a lower thermal conductivity. It is possible that some prejudice against the use of textile materials may be based on the possibility of their being subject to decay either through the agency of bacteria or mould fungi. A further objection might be raised that they are liable to harbour vermin in the form of moths and similar insects. Recent research has shown that mildew will not take place in clean wool unless the atmosphere in which the wool is situated is 97% saturated with water. Bacteria flourish under still more moist conditions. Neither of these sources need be considered in ordinary refrigeration practice, but as a safeguard, if 0.5% of sodium fluosilicate is applied to the wool from solution, this forms an effcient antiseptic.

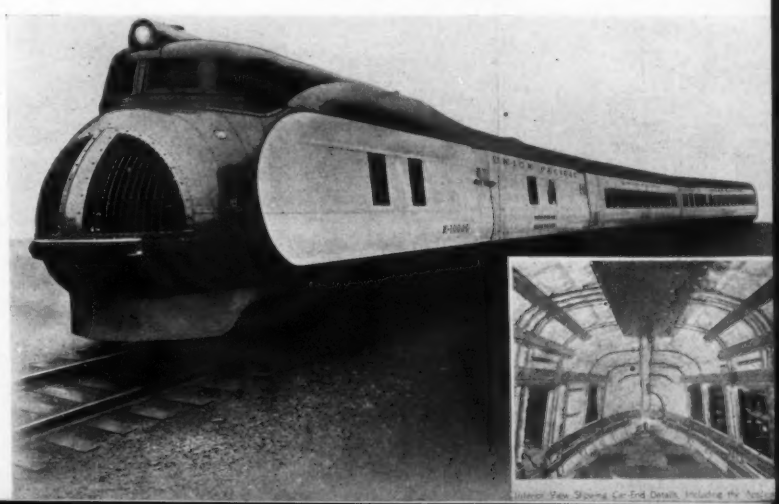
"The cost of using textile materials should not be a serious factor as new wool is not required. A low grade of shoddy properly cleaned is all that is necessary. The presence of a little cotton is not detrimental to the efficiency of the insulator."

Referring to the possibility of the use of shoddy wool in a commercial heat insulator the writer is aware of but one very small application of shoddy card sweepings which is used in conjunction with jute as an insulator.

Asbestos, the mineral fiber which has found varied use in textiles to lend fire proofing and toughness to them, is found in many commercial insulators due to its non-susceptibility to excessive heat. In this respect it is used extensively as an outer layer for textile insulating materials for protection from flames. The insulation selected for the new stream lined Union Pacific train contains closely interwoven mineral fibers backed on both sides with an asbestos open weave cloth.

In general, it may be said that the animal fibers of the textile group possess the best insulating properties, being only outranked by kapok of the vegetable fiber group in this respect. Amongst the majority of commercial insulating bodies, animal fibers are more effective as insulating bodies than mineral matter. In many instances, fibrous

Union Pacific Streamlined Train



mineral matter is mixed with a textile fiber such as flax to increase its insulating properties. One disadvantage of mineral fibers for railroad cars is in their inertness, as compared to the springiness of an animal fiber, which causes it to be shaken down by the jostling of the cars in motion.

A prevalent general opinion is that textile fibers are less durable than other insulators under varied atmospheric conditions. Yet, in many instances, railroad cars having cattle hair as insulation, after being in service for thirty years have been dismantled and the hair found to be in good condition. Many of the mineral fibers on exposure to moisture lose much of their insulating values.

The chief disadvantage of textile fibers as compared to mineral fibers is the fact that they are more inflammable. The animal fibers show the least susceptibility of the group.

Table 2 shows a general description of commercial insulating materials containing textile fibers. This table also gives a comparison of their thermal conductivities with insulating materials of other components. It will be noted that in general the thermal conductivity coefficients are low for those containing textile fibers.

The manner in which cattle hair and jute is used and processed for preparing insulating materials should prove of interest to many who are unfamiliar with this interesting manufacturing process. The procedure is somewhat out of the general manufacturing methods utilized in the textile industry since there is absolutely no weaving in the process.

Table II

Material	*Description*	*Density in lbs. per cu. ft.*	*Thermal Conductivity*
Dry Zero	Grained ceiba fiber between burlap or moisture proof paper	1.0	0.24
Hair Felt	Felted Cattle Hair	13.0	0.26
Hairinsul	75% Hair—25% jute	6.3	0.27
Jute Felt	100% Jute between paper	8.3	0.27
Linofelt	Flax fibers between paper	4.9	0.28
Thermofelt	Jute and Asbestos fibers felted	10.0	0.38
	Cattle Hair Asbestos fibers felted	7.8	0.28
Flaxinum	Loose flax fiber	13.0	0.31
Fibrofelt	Flax and rye fiber	13.6	0.32
Sil-o-cel	Powdered diatomaceous earth	10.6	0.31
Rock Wool	Fibrous material made from rock	10.0	0.27
Eureka	Corkboard with asphaltic binder	14.5	0.32
Lith	Board containing rock wool, flax and straw pulp	14.3	0.40
Insulite	Wood pulp	16.2	0.34
Celotex	Sugar cane fiber	14.8	0.34

The cattle hair which has previously been sterilized is run through a picker or breaker from whence it is blown to the feeding bins of a garnetting or coarse carding machine. The carded hair travels in a continuous broad web from the card to a traveling apron which builds by a shuttle motion a layer upon a layer to form a bat. The latter then is carried under a punching board which consists of a wide board containing close to one thousand long needles beveled at the end to cling to the hair. The board moves up and down at a terrific speed. The bat is carried upon burlap under the board and by the punching action the hairs fasten themselves to the burlap. This is repeated until the required thickness and density results.

Another method of preparing similar insulating material is to run the hair through a carding machine of the Blemeyer type and a bat of a desired thickness is made. The bat is then subjected to the hardening action of a plate hardener after the fashion in which pressed wool felt is made. After the proper thickness and density is attained the material is then dried.

Material of this type is often used as under carpeting in railroad cars. Hairfelt finds extensive use as an insulating body for hot water pipe coverings.

Textile fibers have found an outlet for application in the field of thermal insulation. With the advent of air conditioning in homes there is little doubt but what much further use will be found for textile fibers amongst the heat insulating bodies under development, for tempering the atmospheres of the modern home.

TECHNICAL NOTES FROM FOREIGN SOURCES

Developed Dyeings (Azo); German Patent No. 466,033 *(29/IX/'28)—Dr. Hans Bucherer, Munich.*—The process here protected consists in the use of 2-naphthol-1-sulfonic acid, coupled with a diazotized amine to form a diazo-oxy compound, which is located upon the weave either by printing on as a suitably prepared paste, or by successive impregnations of the goods in baths of the naphthol-sulfonic acid and of the diazo salt. This diazo-oxy compound is then rearranged to the ordinary type of azo compound, by passage through a mineral acid bath, without previous hot-drying or steaming—simply cold drying.

There are involved some points which are of decided interest. Such diazo-oxy couplings are generally considered as nuisances, in the production of azo dyestuffs in substance—they arise, frequently, in couplings where a phenol or naphthol is gotten into solution by means of caustic alkali; they are generally dull in color, frequently merely dirty brown in color, and, involuntarily and unavoidably produced in small quantity along with the desired azo dyestuff, modify the color of the desired product more or less seriously, unless removed in some way before precipitation of the dyestuff by salt. They are in general very resistant to the action of mineral acids (are inconvertible to the desired normal product) or are so labile that they break up quickly in other directions than the desired one.

(Continued on page 448)

The Purification and Properties of Congo Red*

By L. R. PARKS and M. P. KELLER

Congo Red, discovered in 1884 by Bottiger, was the first substantive or direct cotton dye. Due to the peculiar nature of the di-azo dye, it is continuing to stimulate a great amount of research, but its value as a commercial product is decreasing; and today, the dye seems to be finding a place in Biological Chemistry.

It is the purpose of this paper to discuss methods of purifying Congo Red from the commercially prepared product, to study its properties—especially as these properties change with hydrogen ion concentration—and finally to present a simple method for purifying the dye.

Apparatus and Materials

THE dye used in these experiments was Concentrated Congo Red 5T, a commercial product furnished through the courtesy of J. Carl Schmidt, Sales Division, E. I. Du Pont de Nemours and Company. The stick antimony electrode[1,2] was used to determine the concentration of the hydrogen ion of solutions and water. The water was collected from a Barnstead still and ranged in pH from 5.2 to 5.82. The Cottrell molecular weight apparatus modified by Davis[3] was used to determine the rise in boiling point caused by impurities in the dye.

For electro-dialysis the apparatus consisted of two parchment membrane tubes one end of each being fitted with a two-hole rubber stopper containing an inlet tube, a syphon, and a coiled platinum electrode. The electrodes were held in the stopper in such a way that they would not touch the sides of the parchment tubing. Dialysis with water was carried out by placing a synthetic sausage skin containing the dye solution in a vessel, through which water flowed continuously.

Experimental Work

As Congo Red is a colloidal substance one would expect all of the electrolytes in the commercially prepared product to be removed by dialysis. Consequently, the following experiments in electrodialysis and dialysis with water were carried out before the "recrystallization" method was attempted.

A. Electrodialysis of a 2% Solution of Congo Red

Two liters of a 2% solution of Congo Red were placed in a three-liter beaker containing two fitted parchment tubes. The apparatus was adjusted so that water at 58° C. flowed continuously and at a fairly constant rate for twelve hours from the Barnstead still into the supply bottle and through each parchment tube. The syphons kept the level of the water in the tubes the same as the level of the dye solution. The electrodes were connected to the direct current and samples were taken at stated intervals from the dye solution and the water flowing from each parchment tube. The pH value of each sample was determined with the antimony electrode and the samples from the cathode portion were tested with barium chloride and silver nitrate for sulfate and chloride ions, respectively.

It was found that the dyebath dropped in pH from 7.41 to 2.70 during the first half hour. At the end of the first fifteen minute period, the dye solution became very cloudy and blue. On continuing the dialysis a very fine muddy blue precipitate, which did not settle as long as water was running through the parchment tubes, was formed and the pH value of the dyebath dropped very rapidly until a wave of ammonia gas passed through the laboratory causing the dye solution to become a clear red and the pH values of the dyebath to rise instantly to 6.33. This shows how easily affected the dye is by a change in hydrogen ion concentration. At the end of twelve hours the dyebath seemed to have reached a constant pH, 2.37, and no positive tests were obtained for either sulfate or chloride ions. After this experiment had run for about a week the following points were noted If the direct current was left on for a period of twelve hours and the water in the tubes was not changed, a sample of the water from the tube containing the positive electrode gave a heavy precipitate with $BaCl_2$ (which did not dissolve in HCl) and no precipitate with $AgNO_3$ showing that the dye was being decomposed. During this twelve hour period the blue precipitate showed a decided tendency to set-

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*Contribution from the Pond Chemical Laboratories of The Pennsylvania State College.

[1] Parks and Beard, J. A. C. S., *54*, 856-864 (1932).

[2] Parks and Beard, "pH of Dyebaths by the Antimony Electrode" American Dyestuff Reporter *21*, 432 (1932).

[3] Bancroft and Davis, J. Phys. Chem. *33* 591-604 (1929).

tle leaving a practically colorless solution above the precipitate. This effect is similar to that obtained by adding small amounts of acid to a solution of the pure acid dye.

B. Dialysis with water.

A sausage skin of liter capacity containing 400 mls. of a 5% solution of Congo Red was put in a 3 liter beaker, through which distilled water at 80° C. flowed continuously. The results show a drop in pH of the dye solution from 9.1 to 5.09 after 16 hours and to 3.74 after 24 hours. A duplicate experiment was carried out at 58° C. for 18 hours. The pH of this dye solution dropped from 9.08 to 5.48 in 16 hours and 5.26 in 18 hours. The original clear red solution became cloudy and dark violet in color as the pH dropped.

Since the results of dialysis show that the pH of the dye solution probably passed through the neutral point, an electrometric titration of the acid was carried out to determine the strength of the acid. The acid dye—Congo Blue acid—was prepared by adding an excess of hydrochloric acid to the commercial dye, refluxing at the boiling point for one-half hour, washing by decantation, and dialyzing in a sausage skin with hot running distilled water until the wash water was free of the chloride ion. The dialysis was continued for 15 additional hours. On suspending the sausage skin containing the acid dye in a beaker of water having a pH of 5.46 for 12 hours, the pH of the water changed to 5.18 (a drop of 0.3 of a pH) showing that very little hydrochloric acid remained in the acid dye. Aliquot portions of the colloidal solution were titrated electrometrically with 0.005 N sodium hydroxide. The titration curve showed only one break and that a sharp one. Thus Congo Red is a salt of a fairly strong acid; and such a salt when dissolved in water should show about the same pH as that of water.

Dialysis giving uncertain results, a modification of the "recrystallization" method suggested by Hunter[4] was used. The dye was dissolved in hot distilled water and alcohol—ratio 10 grams of dye to 150 mls. of water and 150 mls. of 95% alcohol. The mixture was heated to boiling and filtered while hot through a Buchner funnel. The filtrate was set aside to cool for 24 hours during which time the precipitate forms. The dark reddish product was filtered off by suction and washed with cold 95% alcohol. The recrystallization was carried out four times. To obtain the product in a granular form the purified dye was covered with hot 95% alcohol, digested for a few minutes on a hot plate and filtered.

Since the boiling-point of a colloidal solution[5] is very slightly different from that of water, the presence of a small amount of inorganic salt may be detected by a rise in boiling point. The rise in boiling point was determined according to the method suggested by Davis[6]. Three grams of dye were taken at various times during the recrystallization process and added to 150 mls. of water. The rise in boiling point obtained from these solutions showed a decrease from 0.127° to 0.001°, the latter being the average of three determinations. Each boiling point determination represents an average of 50 readings on the water and the dye solution. In each case corrections were made for any change in barometric pressure.

The purity of the dye was further tested by conductivity measurements. A 0.001 N. solution gave a specific conductance of 92.4×10^{-6} at 25° C. It should be noted that Schramek and Gotte[7] who state that pure substantive dyes cannot be prepared from the commercial product obtained a slightly higher value for the specific conductance of their pure dye. It is possible that the method of dialysis they used did not remove the last traces of electrolytes. However, using for the equivalent conductance at infinite dilution their value, 106, calculations show that a 0.001 N solution of this salt is 87% ionized. The percent of sodium was determined as sodium sulfate and found to be 6.51%. The calculated value is 6.61%.

When pure Congo Red was dissolved in water with a pH of 5.82, the pH values increased from 6.01 when 32.6 mgs. of dye were dissolved in 250 mls. of water to 6.65 when 522.1 mgs. of dye were dissolved in the same amount of water.

An aqueous solution of Congo Red shows some tendency for a small amount of the dye to settle out. Mr. H. W. Wright of these laboratories has been measuring particle size of dyestuffs using the Zeiss Slit ultra-microscope and states that the size of the completely dispersed colloidal particle of Congo Red is very small, and that only a few are seen in vigorous Brownian movement. However, a few larger particles are seen which are probably between those finely dispersed and the particles large enough to precipitate out. Mr. Wright further states that dilute solutions of sodium hydroxide disperse these larger particles up to a concentration of 0.006N. Measurements were not made beyond this point.

Congo Red is very sensitive to acids. In the presence of an excess of strong mineral acids, like hydrochloric acid, the Congo Blue acid flocculates leaving a clear colorless solution. On removing the excess mineral acid by dialysis, the acid dye is dispersed and forms a stable colloidal solution. Carbonic acid will partially precipitate the dye, leaving the solution cloudy and deep red violet in color. On boiling or bubbling air free of carbon dioxide through the solution, the carbon dioxide is driven off and the dye regains the same clear red color and pH as an untreated solution.

By controlling the concentration[8] of the hydrogen ion in the dyebath of Congo Blue acid it is possible to dye samples of standardized cotton blue, lavender, pink or red. The color of a dyed sample of cotton can be changed

[4] Hunter, Biological Journal, *10*, 42-46 (1934).
[5] Thorpe, "Dictionary of Applied Chemistry," Longmans, Green and Company, 336 (1921).
[6] Loc. Cit.
[7] Schramek and Gotte, Kolloid Beikefte, *34*, 218-269 (1931).
[8] Parks and Keller, Am. Dyestuff Reporter, *23*, 83, (1934).

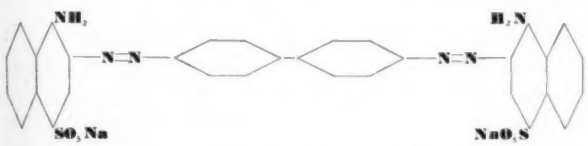
from red to blue by exposing the sample to a volatile acid or immersing it in an acid solution. The red color may be restored by exposing the blue sample to a volatile base or immersing it in a basic solution.

Discussion

The colloidal property of a solution of Congo Red is revealed when the dye will not diffuse through a sausage skin or parchment paper during dialysis or noticeably raise the boiling point of the dye solution from that of water[9].

states that the optical properties of an aqueous solution of Congo Red show that it is colloidal. Zsigmondy[10] states that ultrafiltration of solutions of Benzopurpin 4B and Congo Red shows that Benzopurpin exists in larger particles than Congo Red, but finer than any type of gold particles. The colloidal solution is charged negatively[11,12]. Congo Blue acid forms a negative colloidal solution containing particles sufficiently large and anhydrous to be visible in the ultramicroscope[13,14].

The dye is placed on the market as the sodium salt of diphenyl - dis - azo - bis - a - naphthylamine-4-sulfonic acid, usually assigned the following structural formula:



For convenience the formula of Congo Red will be written as Na_2R, where R represents the acid radical.

Measurements of osmotic pressure, freezing point[15,16] lowering, and boiling point raising of aqueous solutions of Congo Red indicate that the dye behaves as a non-electrolyte. However, conductivity measurements show that the dye is composed of highly ionized aggregates or micelles. Since evidence points to the fact that the dye is polymerized and ionized, the ionic equilibrium should be written $(Na_2R) = (Na_2R)_{x-n}.n\ (NaR)^- + n^+$, until methods are perfected to determine x and n.

Although an electrometric titration shows Congo Red to be the salt of a fairly strong acid, the pH values of solutions of this dye increase with the concentration of the solution. This would indicate that the dye hydrolyzes basic to a slight extent.

An examination of the structural formula of Congo Red indicates that an acid might react with it in two places forming an addition product with the amino groups or a substitution product, in which hydrogen atoms of the acid replace the sodium atoms of the dye. An analysis of pure Congo Blue acid shows the presence of neither sodium, chlorine, nor hydrochloric acid.[17,18]. Therefore, it can be concluded that the reaction is substitution and that the amino groups are weakly basic.

Heat causes the colloidal particles to disperse and become smaller. Livet[19] further states that particles of different sizes are not equally colored. Weiser and Radcliffe[20] carried out experiments studying the effect of heat on solutions containing varying concentrations of Congo Blue acid and concluded that the Congo Blue acid is slightly soluble in water yielding the red colloidal anion. The solubility is increased with rise of temperature, giving colors varying from blue to red. They consider that the blue color is due to the non-dissociated acid while the red color is that of the anions. Conductivity measurements show that the acid dye is ionized, therefore by increasing, the concentration of the hydrogen ion the equilibrium is displaced toward the non-dissociated and polymerized acid, which will give cotton a color varying from red to blue. Therefore, any process which will tend to increase the particle size of Congo Blue acid will produce colors of a blue shade, while those which tend to decrease the particle size produce colors of a red shade. In other words, the color developed on the fiber is dependent upon the particle size of the Congo Blue acid in the dyebath.

The tendency of Congo Red to precipitate out on standing may be due to the carbon dioxide[21] in the solution forming the acid dye, which displaces the carbon dioxide equilibrium between the air and the solution, causing a new equilibrium to be set up between the air, dye solution, and acid dye. On boiling or bubbling air free of carbon dioxide through the solution, the acid dye is decomposed and part of the carbon dioxide is liberated which displaces the equilibrium in the opposite direction.

In water solution Congo Red ionizes to give the anion and sodium ion. During the process of dialysis the sodium ion is washed out along with hydroxyl ions thus leaving the acid dye. Although carbon dioxide is not the cause of this reaction, the presence of carbonic acid increases the concentration of the hydrogen ion and tends to shift the equilibrium toward the formation of the acid dye and in that way hasten the dialysis toward the acid side.

Dialysis is affected by so many factors, namely: type of dialysis, temperature, time, and carbon dioxide, that the results are uncertain and cannot be duplicated—especially with reference to pH values. Consequently, the "recrystallization" method presented in this paper for purifying Congo Red is the most satisfactory since the results are easily duplicated.

Summary

1. Congo Red cannot be purified by dialysis.

2. Commercially prepared Congo Red can be purified satisfactorily by the "recrystallization" method presented in this paper.

[9] Livet, Tiba, *8*, 391-397 (1930).
[10] Zsigmondy, Chem. Abst., *19*, 1079 (1925).
[11] Briggs, J., Phys. Chem., *28*, 368-386 (1934).
[12] Ostwald, Chem. Abst., *13*, 2625 (1919).
[13] Bayliss, Proc. Roy. Soc., London, (B) *81*, 269-286 (1907).
[14] Fay, Tag, and Hawkins, Chem. Abst., *6*, 156 (1912).
[15] Bayliss, Proc. Roy. Soc., London, (B) *81*, 269-286 (1907).
[16] Zsigmondy, Chem. Abst., *19*, 1079 (1925).
[17] Fay, Tag, and Hawkins, Chem. Abst., *6*, 156 (1912).
[18] Bogoyavlenskii, Chem. Abst., *7*, 1172 (1913).
[19] Livet, Tiba, *8*, 651-663 (1930).
[20] Weiser and Radcliffe, J. Phys. Chem., *33* 1876-1885 (1928).
[21] Kendall, J. A. C. S., *38*, 2460 (1916).

3. An electrometric titration of Congo Blue acid shows one sharp break.

4. A solution of Congo Red (0.001 N) is 87% ionized and has a specific conductivity of 92.4 x 10^{-6} at 25° C.

5. In solution Congo Red hydrolyzes to a slight degree.

6. Carbon dioxide will change a solution to the dye from clear red to cloudy dark red violet. The carbon dioxide can be removed as shown by pH values.

7. By controlling pH, standard cotton can be dyed with Congo Blue acid any color from blue to red.

TECHNICAL NOTES

(Continued from page 444)

Dyeing of Cellulose Esters and Ethers (Developing on Fiber); German Patent No. 468,210 (8/*XI*/'28) (*addition to G. P. No.* 467,036 *of* 1/*I*/'28)—*I. G. Farben—Ind. A. G.*—The original patent covers the use of dyestuffs obtained by coupling of non-sulfonated diazo-salts with 2-4-diaminophenyl-methane-sulphonic acid, for the dyeing of cellulose esters and ethers. The present additional patent covers the extension of such dyeings by aftertreatment with suitable diazo-salts thereby attaining deeper and faster tones. Two examples are given.

Example 1—by coupling diazotized aniline to 2-4-diaminophenyl-methane-sulfonic acid, a dyestuff is obtained which dyes acetate silk a straw color. This dyeing, if aftertreated in a bath of diazotized p-nitroaniline, goes over to a yellowish brown.

Example 2—by coupling diazotized alpha-naphthylamine to the same second component, an orange dyeing is obtained, which by aftertreatment with diazotized p-nitraniline, goes over to a reddish brown.

The Latest Explanation of Felting

IT is believed that this note can be correctly described as the latest important contribution to the explanation of the felting of wool. According to A. T. King, who is working in close association with the British Wool Industries Research Association and with other leading investigators of wool, the most important factor in felting is the "unique reversible extensibility common to the keratin class of fiber." The different degrees of felting of different wools depend upon secondary effects some of which have heretofore been given first place in the explanations of felting. Such are scale and contour characteristics and fiber length.

The felting effect is supposed to be due primarily to the continuous (alternate) stretching and recovery of the wool fibers during the mechanical action. Since fulling mills are designed to exert pressure, the stretching is an indirect effect. If a machine is designed to produce both stretching and compression it will felt wool more rapidly.

While the so-called interlocking scale theory has been pretty generally discarded, the scales are still important. They interlock while the fibers are in the stretched state and draw the fibers closer together during the recovery of length. There would be the most effective felting when these two effects of stretching and contracting are properly balanced at their "maximum" values.

The correct balance is effected by the adjustment of pH. Felting effects are at a minimum within the pH range 4 to 8 because the ease of extension is at a minimum although the power of recovery would be at its greatest. An increase in alkalinity increases the stretchability but at the same time cuts down the power of recovery. The most favorable point has been found to be at a pH of 10. Felting is slower because of a lower extensibility below this point, and slower because of less power of recovery above this pH.

Felting is then the result of something very much in the nature of an attack on the wool substance. According to modern views, largely those of Astbury, the stretching of the wool fiber which is fundamental to fulling is due to the straightening out under tension of the coiled or wavy molecular chains which extend lengthwise of the fibers. These chains are held in their folded positions by cross linkages between those chains which adjoin. These offer resistance to stretching and exert forces for recovery. These links are broken with an increase in alkalinity but at the proper pH the breakdown which allows easier stretching is carried only to a point where there is still a sufficient recovery force to perform its part of the process.

Incidentally, it has been reported by the director of the Wool Industries Research Association that the study of mechanism and effect on wool of the felting process has shown that the application of a simple and inexpensive treatment during processing will cut down the time required for fulling, by as much as one-half in some cases. The exact nature of this treatment has apparently not been made public. (Main reference Chemistry and Industry *53*, 339 and 340).

However, from another source comes the information that a machine has been made to exert both stretching and compressing forces on goods during fulling by means of a pair of rollers at the spout of the fulling mill, driven in the opposite direction to the movement of the cloth. The goods are pulled against this resistance and the result on certain classes of union goods has been a great reduction in the time required. This is probably the treatment mentioned above and it would seem to represent a great advance in the art of fulling.

OPEN FORUM

Rules under which this department of the REPORTER is conducted are as follows:

1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.

2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.

3. For each such reply published the Reporter will pay a minimum of $2.

4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.

5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.

6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.

Answers

5.—We are interested in obtaining some information on the reaction of rayon to dyestuffs in comparison to silk, cotton, wool and linen. Can you set us straight on the following points?

A. Does rayon take dyes more easily than any, or all, of these?

B. Does rayon take truer colors of dye?

C. Does it take dyes more evenly?

D. Does it retain colors longer?

E. Can a greater range of color variation be obtained in dyeing rayon? More subtle colors? More brilliant?—**M. J.**

In presenting the following letter and further answer to question No. 5, the Reporter wishes to again call attention, and emphasize rule No. 5 as published in the heading of the Open Forum.

Answer No. 2:—

Dear Editor:

In answer to your letter of the sixth, attached is some information relative to question 5 in the May 21 issue of the American Dyestuff Reporter.

The writer has no special desire to answer general questions, but just rather felt that when a man asks a question it is unfortunate that his question is called absurd.

We more than agree with you that you cannot accept or assume any responsibility for answers, but it would seem natural when a man wants dyeing information he would turn to a technical or chemical magazine and expect a courteous and accurate answer. To question D the man gets no answer at all with the exception of an evasive reply, whereas it is well known that colors on rayon are faster to both light and washing than the same colors on cotton.

It is not entirely plain just what the person in question has in mind and it would be interesting to get in touch with him, because whether his answer should be rayon and the other fibers mentioned alone, or whether he has in mind combining rayon with other fibers.

The writer had in mind it might be helpful to the magazine to draw to your attention an answer to a question that is not an answer, because if the Open Forum is going to have any value certainly a person should be able to depend on the accuracy of the answer.

(A) The different fibers mentioned need separate lines of dyestuffs to properly color them. Rayon, cotton, and linen are dyed mostly with the direct cotton colors, vat colors and sulfur colors; whereas on silk and wool the dyers use mostly acid and chrome colors.

You may have in mind combining some of these fibers; and if so, in a mixture of rayon and cotton, the rayon would, generally speaking, be dyed very much heavier than the cotton. There are special colors and special handling that will bring these two about the same strength, but in just ordinary dyeing, as stated above, the rayon will be much heavier than cotton.

In combining rayon with wool, or cotton with wool in using union colors, the rayon would dye heavier than the cotton.

(B) We would not make a specific answer to this question as to whether rayon takes truer colors of dye. We can only say colors on rayon are much brighter than those on cotton on account of the rayon fiber being bright and more lustrous.

(C) It is more trouble to dye rayon even than any of the other fibers and even separate shipments of rayon from the same manufacturer will dye differently. You can take sometimes two types of rayon, one which we call fast dyeing and one slow dyeing, and by putting them into the same dyepot one will dye much heavier than the other.

(D) The same dyestuff on rayon and cotton in many instances would be faster to both light and washing on rayon than it is on cotton.

(E) A great range of colors can be dyed on all fibers, but as mentioned above the dyeings of rayon look more brilliant on account of the fiber itself.

There are so many variations possible as regards methods of dyeing that your questions could be best answered by a personal conversation. To be specific, the ordinary cotton colors are used for rayon, but there are some special formulae whereby acid colors can be dyed on the rayon.—W. C. S.

New Question

17.—We are in need of mathematical text books on problems pertaining directly to textile printing but so far have been unable to find anything on the subject. If you know of texts or problems in math. especially adapted to this field, I would more than appreciate suggestions.—**O. E. M.**

● CORRECTION

"Analysis of Dye Mixtures", Page 722, Dec. 4, 1933.

Page 725—Column 1, line 8 from bottom reads—"with 30 cc 1:1 and aniline-amyl alcohol mixture that" Delete the word "and" from this sentence.

Page 725—Column 2, line 17 from top. The last word of this line should be "solution" instead of "section".

Page 745—Line 4 from top in first column. The number preceding the words "Acid Black" should be "246" instead of "240".

Page 745—Lines 23 and 24 from top read—"Dyes of group 9. Amounts extracted by aniline, and by 1:1 aniline-amyl alcohol mixture." Add to the last sentence the words "from solutions in normal potassium hydroxide".

Page 745—Column 2, lines 21, 22, and 23 from bottom of page read—"U. S. Dept. Agr. Bull. No. 448. Jour. Ind. Eng. Chem., *5* U. S. Dept. Agr. Bur. Chem. (1913). *26* and *12* (1920) 883. Circ. 113."

Change this to read—"U. S. Dept. Agr. Bull. No. 448. Jour. Ind. Eng. Chem. *5*, (1913), *26*, and *12*, (1920), 883. U. S. Dept. Agr. Bur. Chem. Circ. 113."

Page 745—Line 8 from bottom of page, in second column of table, reads—"1/64-Normal Acid".

Change to read—"4-Normal Acid".

Page 745—Line 8 from bottom of page, in fourth column of table, reads—"4-Normal Acid".

Change to read—"1/64-Normal Acid".

● REESER RETURNS

M. D. Reeser, of the Howes Publishing Company, has returned to the office after an absence of two months due to severe illness.

● GENERAL RELEASE

The General Dyestuff Corporation has released a circular on Leophen B,—a new mercerizing assistant. It is a pale yellowish, practically odorless liquid said to be free from cresol which dissolves readily in mercerizing liquors. It is non-poisonous and practically free from frothing. On account of its penetrating properties, yarns and pieces may be mercerized without previous boiling out.

● R & H PRICE LIST

The R & H Chemicals Department of E. I. duPont de Nemours & Co., Inc. has released its July "Quarterly Price List". Copies are available on request.

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

POSITION WANTED: Research and plant chemist, rayon processing man, with over ten years of practical experience with leading American and European dyeing and finishing organizations, presently on a business trip in Europe, will be available at the end of September. Write Box No. 818, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

POSITION WANTED: Experienced chemist, intermediates and dyes recently printing colors desires connection. Write Box No. 821, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.

WANTED: Old established New York Dyestuff House has opening for firstclass salesman with following in Philadelphia territory. Give full particulars. Confidential. Write Box No. 823, American Dyestuff Reporter, 440 Fourth Avenue, New York, N. Y.